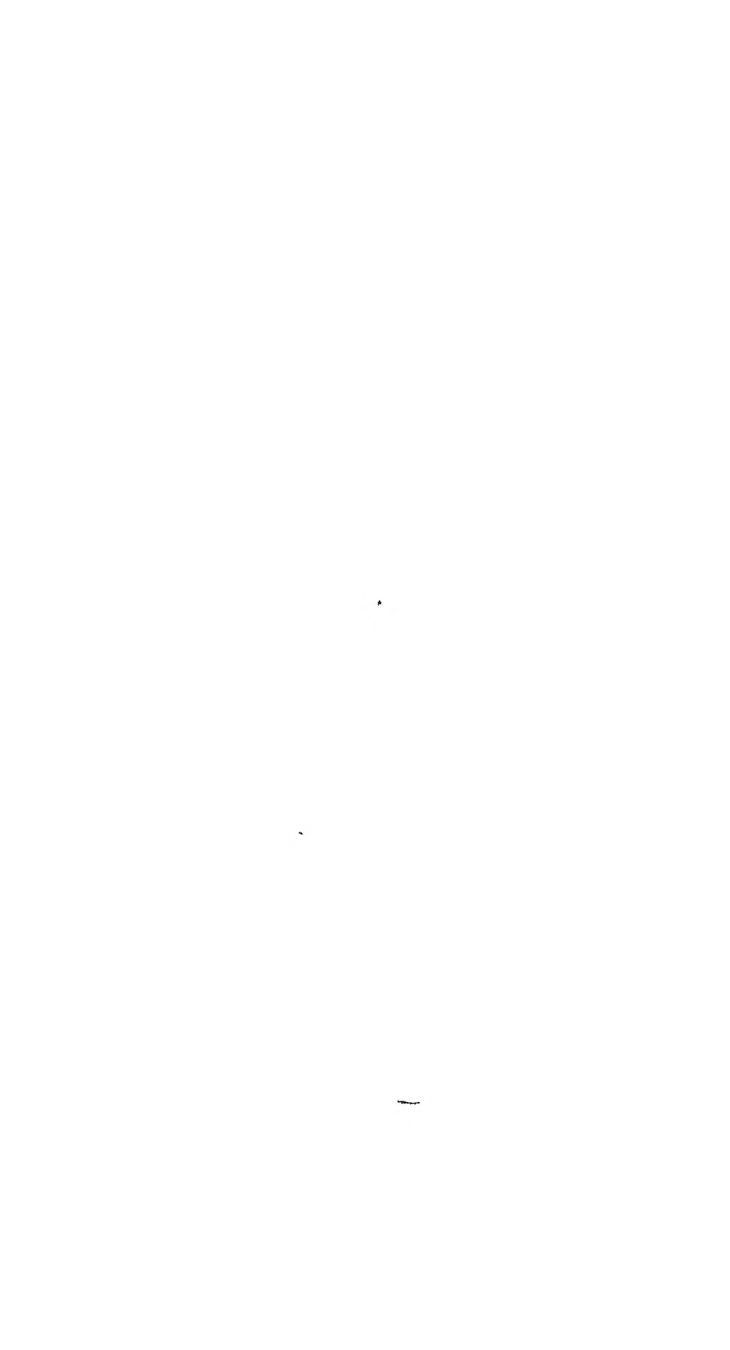


# CHEMISTRY & ATOMIC STRUCTURE



# CHEMISTRY & ATOMIC STRUCTURE

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DEDICATED TO THE MEMORY OF  
ALFRED WERNER  
NOBEL LAUREATE  
PROFESSOR OF CHEMISTRY, ZURICH  
FOUNDER OF THE  
CO-ORDINATION THEORY  
OF  
ATOMIC VALENCY AND MOLECULAR CONSTITUTION



## INTRODUCTION

THE rapid development of subatomic physics in recent years has been accompanied by the promulgation of many theories as to the ultimate structure of matter, and these conceptions, although perfectly legitimate as working hypotheses, are nevertheless often regarded as proven facts, especially by those chemists who are too much engrossed in their professional studies to follow critically the trend of modern physical research into the nature of atoms. Yet it must be conceded that the acid test of the validity of these speculations is, do they classify, correlate and explain the known facts of chemical science.

In *Chemistry and Atomic Structure* the author, Dr. J. D. Mann Smith, who has devoted much time, labour, and research to the subject, has applied this criterion to the various theories which have at different times received acceptance since the foundation of chemistry to the present day.

As the almost inevitable result of the rapid and increasing advance of knowledge in physics and chemistry, students are tempted more and more to hurry over the fundamental concepts of these sciences in order to gain a superficial acquaintance with recently discovered phenomena. The author corrects this unfortunate tendency by devoting the opening chapters of his treatise to the fundamental topics of atoms, molecules, valency, electrochemistry, and the classification of the elements. A survey of the growth of modern chemical science shows that on these sound foundations has gradually been erected the solid structure of three-dimensional chemistry, arising out of an intensive cultivation of carbon derivatives, then extending to compounds of other elements and embracing more complicated types of molecular architecture.

To the texture and grain of this molecular fabric modern physics has applied the refined methods of X-ray and positive ray analysis and the powerful weapons furnished by radioactive matter, with the result that much of the inner mechanism of the chemical atom has been revealed.

These epoch-making discoveries necessitate an amended description of the phenomena of chemical valency and combination in terms of the electronic theory of atomic structure. The conception of atoms as the domains of dynamic electrons is now shown to be compatible with the facts of chemical combination and stereo-isomerism.

This treatise, which is dedicated to the memory of the Founder of the co-ordination theory of atomic valency and molecular constitution, furnishes a concise and logical exposition of Werner's original hypotheses and brings these conceptions into line with recent experimental evidence and modern philosophic thought.

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DEPARTMENT OF CHEMISTRY  
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*October, 1924*

## PREFACE

UNTIL comparatively recent years the theory of atoms was entirely a chemical theory, neither particularly useful nor necessary in physics. The last generation, however, has witnessed the development of a physical theory of atomic structure more complete than ever had appeared possible in chemistry, and it has lately been customary to regard chemistry as concerned only with the superficial structure of atoms.

Consideration of the enormously varied and minutely diversified chemical properties of the colossal number of known chemical compounds brings the conviction that the outer structure of atoms is insufficient for an explanation and that chemistry is fundamentally concerned with the structure of atoms even to the heart of the nucleus. Chemistry and physics must, therefore, be regarded as complementary sciences, overlapping at the same point as the classical and quantum theories of physics overlap, at the surface of the atom.

I have endeavoured to maintain throughout as self-detached a point of view as possible in the presentation of historical facts and the exposition of views and theories, while maintaining as independent a point of view as possible in the critical review of hypotheses and interpretations of experimental facts.

I have not scrupled to introduce new and perhaps strange ideas, as additional or supplemental explanations of both simple and abstruse problems and phenomena. I do not, however, wish to appear to have grafted on to the work of others views foreign to their intention, and, in case it may not always appear from the text, I hold myself responsible for the following, the generalisations of Werner's co-ordination theory; the classification and tables for the isomerism of tetrahedral, octahedral, and cubic co-ordination complexes; the criticism of Werner's nomenclature, the interpretation of electronic structures from radioactivity phenomena; the criticism of the actinium series atomic weights; the detailed calculations of Moseley's "screening

## *Chemistry and Atomic Structure*

constants", the criticism of the fractional atomic weight of hydrogen, and artificial disintegrations; the ether mechanism for energy exchange between light waves and electrons and for the non-radiative properties of Bohr orbits; the criticism of the "relativity effect"; the proposal of spatial precession domains for elliptic orbits for both free and combined atoms; the criticism of the covalency bond of two electrons; the proposal of the law of uniform atomic plan, the interpretation of chemical evidence in terms of electron subgroup structure; and the detailed structures assigned to elements generally.

I wish to express a great indebtedness to the work and ideas of the late Professor Alfred Werner and Professor G. T. Morgan in chemistry, and of Sir Oliver Lodge, Professors N. Bohr and A. Sommerfeld, Sir J. J. Thomson, and Sir Ernest Rutherford in physics and the borderland of physics and chemistry, and to acknowledge the unfailing general and generous assistance of H. M. Department of Scientific and Industrial Research.

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The contractions used in the references to original papers are, in nearly all cases, those used in the Abstracts of Chemical Papers issued by the Bureau of Chemical Abstracts

## CHAPTER I

### ATOMS

SPECULATIONS as to the ultimate causes and origins of material phenomena usually resolve into notions regarding infinity, and fall into two classes, related as proposition and its converse. Matter, for example, may be regarded as continuous or granular. Theories of the continuous nature of matter postulate that any portion of any apparently homogeneous substance is throughout as homogeneous as it appears, and admits of unlimited subdivision without any change in nature appearing. Theories of the granular structure of matter, on the other hand, postulate that any portion of any apparently homogeneous substance is reducible by subdivision to a particle which is either indivisible, or divisible, only with a fundamental change in the nature of the substance into parts consisting of indivisible particles. All atomic theories postulate indivisible ultimate particles, though in chemistry atomic theories relate to particles which are indivisible except with change in properties, and ultimate indivisibility is not postulated.

The earliest recorded system of philosophy, based on an atomistic view of matter, appears to be that of the Hindu philosopher, Kanada, probably earlier than 1000 B.C., who postulated the existence of small particles of matter consisting each of a few ultimate indivisible particles or monads. Kanada's doctrines were early incorporated in the tenets of the various sects of the Buddhist religion, and became widely diffused over Asia.

It has been suggested, and there is considerable evidence of the westward spread of Buddhist doctrines prior and subsequent to the rise of the early Greek civilisation, that the atomistic views of Leucippus, a Greek philosopher of about 450 B.C., and of his pupil Democritus (425 B.C.) are to be ascribed to Buddhist influences. However this may be, it is certain that the atomic hypothesis, usually associated with the name of Democritus, alone has directly influenced western scientific thought since the Renaissance.

The atomistic philosophy of Democritus was modified by Plato, a pupil of Socrates, in the dialogue, the *Timaeus*, about 400 B.C., by grafting on parts of the mathematical and geometrical doctrines of the later Pythagoreans. Plato assigned to the primordial atoms the shapes of the five regular solids, the tetrahedron, octahedron, cube, icosahedron, and dodecahedron, the four, six, eight, twelve, and twenty point symmetrical configurations respectively. The Democritan doctrine was further elaborated by Epicurus (about 300 B.C.) into a comprehensive system of philosophy, though little now remains on record of the Epicurean system except in the poem, *De Rerum Natura*, of the Roman, Lucretius, who lived from about 100-55 B.C.

Aristotle (384-322 B.C.), a pupil of Plato, early abandoned the Platonic system, and founded the Peripatetic school, which rejected the Democritan atomic hypothesis and postulated the infinite divisibility of matter and the transmutation of elementary substances. Owing to the tremendous influence of the Aristotelian school on contemporary and subsequent thought, atomistic doctrines fell into disrepute. Owing further to the fact that chemistry, in the early and middle Christian ages, was almost exclusively an Arabian art founded on the teaching of Aristotle, the atomic view of matter practically disappeared during the sixteen centuries from the time of Lucretius, until the Renaissance brought back the study of the pre-Christian philosophies.

The Democritan doctrine was first revived by Francis Bacon (1561-1626) in his *Novum Organum*, and Gassendi (1592-1655), in his strong opposition to the Aristotelianism of his time, brought forward and adapted the system of Epicurus. Despite a partial set-back, due to the continuous-matter theory of Descartes, known as the Cartesian Philosophy, atomic views of matter became generally accepted. Robert Boyle (1627-1691), in his *Sceptical Chymist* and *The Usefulness of Natural Philosophy*, applied a corpuscular or atomic theory of matter to combination

between substances to form other substances and to a dynamic explanation of gaseous pressure. Isaac Newton (1642-1727), in his *Opticks* and the *Principia*, referred chemical changes to atomic combinations, accepted and developed Boyle's explanation of the cause of gaseous pressure, and applied the atomic hypothesis to the forces of chemical affinity, gravitation, electricity, and magnetism.

In 1776, Bryan Higgins, in his *Philosophic Essay concerning Light*, brought the atomic hypothesis more directly into relation with chemistry, by his suggestion that two different atoms combine singly to form a compound, and William Higgins, in his *Comparative View of the Phlogistic and Antiphlogistic Theories with Inductions* (1789), expanded this suggestion into a definite theory of combination between atoms in multiple proportions, the simplest and stablest combination occurring between two different atoms to form a binary compound.

Though T. Nicholson had defined chemistry in 1795, in his *Dictionary of Chemistry*, as a science of the changes produced in bodies by the movement of parts individually too minute to affect the senses, the atomic view of matter was merely a bare hypothesis, neither necessary nor even convenient for an explanation of chemical facts. Indeed, at the commencement of the nineteenth century no single quantitative phenomenon, relating to the combination of substances either by weight or by volume, had been shown to be in accord with the necessities of an atomic hypothesis. Numerous determinations had been made by weight and by volume of the proportions in which elements combine, but the results had not been applied to the support of the doctrine of atoms, though the Higginses had postulated a theory of chemical combination atom to atom, which was clearly susceptible of quantitative investigation.

As early as 1630, Jean Rey, in an essay, *Investigation of the Cause of the Gain in Weight of Tin and Lead on Calcination*, showed that such gain in weight never exceeded a certain limit. Homburg, in his *Observations on the Quantity*

of *Acids Absorbed by the Alkaline Earths* (1669), determined the amounts of various acids required to "saturate" (neutralise) a fixed amount of "salt of tartar" (potassium carbonate), and his results may be regarded as the first steps towards the establishment of the Law of Equivalent Proportions.

Cavendish, in 1767, and Wenzel, in 1777, indicated that **equivalency** existed between the various weights of metals and bases that neutralise a definite weight of any given acid, and, further, that this equivalency was independent of the particular acid used. The extensive researches of Richter, the originator of the distressful term "stoichiometry"—the quantitative relations between chemically reacting substances—finally established in his *New Arts of Chemistry* (1792–1802), the truth of the foregoing law, frequently called **Richter's Law of Proportionality** or of **Equivalent or Reciprocal Ratios or Proportions**. This law states that **the ratios between the weights of different substances that combine with a constant weight of another substance are either equal to the ratios of the weights of the substances in their combination with each other or are small integral multiples or simple submultiples of these ratios**. Originally applicable to the combination of acids with bases or metals, it was proved by Berzelius<sup>1</sup> to be equally valid for compounds and elements generally, and it is to-day, owing to the extraordinary refinement of atomic weight methods, the most firmly established of the laws of chemistry.

One of the outstanding difficulties in the way of the early general acceptance of Richter's Law lay in the well-known fact that some substances combine in several different proportions with a constant weight of another substance. It was not even certain at the beginning of the nineteenth century that combination between substances did not take place in every sort of continuously varying ratio. The controversy between Berthollet and Proust, as to the fixity

<sup>1</sup> *Gilbert's Ann*, 1811, 37, 248 and 415, 38, 161 and 227, and 1812, 40, 162 and 235

of composition of compounds, lasted from 1802 to 1808, and, though **Proust's Law of Constant Composition** was generally accepted and had in fact been tacitly assumed many years previously by Cavendish, Richter, and Lavoisier, conclusive experimental evidence for it in any great detail was not available until Berzelius from 1810 onwards had determined the exact composition by weight of nearly all the chemical compounds known in his day.

Richter had noticed in 1792 that a metal could form oxides with two different proportions of oxygen, Lavoisier was aware of a number of elements which combined with another element in several different proportions, Cavendish analysed three different oxides of nitrogen; Proust in 1799 analysed two different oxides of copper; Clément and Désormes discovered in 1801 that carbonic acid contained twice as much oxygen as carbonic oxide; and Dalton in 1802 showed that nitric oxide combined with air in two proportions, one double the other.

Whether or not Dalton was aware of the suggestion of W. Higgins, that combination between atoms takes place in multiple proportions, is not known with certainty, but in 1803, fourteen years after the publication of Higgins's suggestion, Dalton brought forward an almost identical theory of atomic combination and devised a system of atomic weights, entirely based on the assumption of combination between atoms in simple multiple proportions. The broad outlines of Dalton's theory were first indicated in Thomson's *System of Chemistry*, published in 1807, and Dalton's celebrated work *A New System of Chemical Philosophy* appeared in 1808, and almost immediately the atomic theory met with general acceptance.

The virtue of Dalton's theory was not that it was an atomic theory, for theories of atoms are far older than the science of chemistry, but that it represented the first definite attempt to place on a quantitative chemical footing the doctrine of combination between elementary corpuscles first laid down by Boyle and later by W. Higgins.

Dalton's atoms, as we now know, were not real atoms, and more nearly coincided with the modern conception of molecules, and his so-called atomic weights were usually sub-multiples of real atomic weights, and were often in fact the modern chemical equivalent weights, which are related to the atomic weights by a simple multiple now called valency or the combining capacity of an atom measured in terms of hydrogen atoms or their equivalent. Dalton's outstanding achievement was his recognition of the **Law of Simple Multiple Proportions by Weight**, which states that the different weights of an element, in combination with a constant weight of another element, are small integral multiples of a common factor.

It appears that Dalton had embraced the theory of atomic combination considerably prior to his recognition of the experimental facts of combination of substances in simple multiple proportions by weight, and that his law as to such combination was deduced from the necessities of an atomic theory. It is certain that much of the evidence on which he relied to support his theory has since been shown to be untrustworthy or susceptible of other conclusions. He showed, for example, that olefiant gas (ethylene) contains twice as great a proportion of carbon as marsh gas (methane). Had ethane been known in his day his theory would have had to be abandoned as soon as proposed, for ethane contains one and one-third times as much carbon as methane, to which Dalton assigned the formula  $\text{CH}_2$ , and two-thirds of that in ethylene, to which Dalton assigned the formula  $\text{CH}$ . In benzene,  $\text{C}_6\text{H}_6$ , naphthalene,  $\text{C}_{10}\text{H}_8$ , anthracene,  $\text{C}_{14}\text{H}_{10}$ , and picene,  $\text{C}_{22}\text{H}_{14}$ , Dalton would have found compounds having weight ratios of hydrogen to carbon of 1, 0.8, 0.714, and 0.836, unreconcilable with his law of simple multiple proportions by weight. It can be regarded only as remarkably fortunate that the few compounds known in Dalton's day were the simpler compounds of chemistry, to which alone the law applies.

The two chief assumptions of Dalton's theory, that combination takes place in simple multiple proportions by weight and that the simplest and stablest compound is a binary combination of one atom with one other atom, are both unjustifiable. The first assumption is validly applicable only to such compounds as are not formed by combination between atoms of the same element. The second assumption is also unwarranted, and in fact led to a confusion in the subsequent half a century almost unparalleled in the history of any science.

As early as 1814 Wollaston clearly saw that it was impossible, in the then existing state of chemical knowledge, to ascertain, in the cases to which the law of simple multiple proportions by weight was applicable, which or if any compounds consisted of one atom of one element combined with one atom of another element. He proposed to discard Dalton's purely hypothetical atomic weights and to substitute equivalent weights,<sup>1</sup> being the experimentally ascertained combining weights of elements referred to a fixed weight of a standard element. Gmelin, in his *Handbuch der Chemie* (1817), was no less clear as to the insecurity of Dalton's atomic weights, and decided in favour of equivalent or combining weights, and Gmelin's system remained in more or less extended use on the Continent for nearly fifty years.

Berzelius, probably the greatest experimental chemical genius of the nineteenth century, adopted Dalton's atomic theory, and proposed the present system of chemical nomenclature,<sup>2</sup> in which the initial letter or the initial letter and another are used to symbolise elements. Owing to the defect in Dalton's theory in that no certain criterion existed for determining the real relative weights of atoms, Berzelius was frequently compelled to alter his scheme of atomic weights, and thereby undermined the foundations

<sup>1</sup> *A Synoptic Scale of Chemical Equivalents*, *Phil Trans R Soc*, 1814, 104, p 1

<sup>2</sup> *Journ. Phys.*, 1811, 73, 257, and *Larbok i Kemien*, 1811

of the atomic theory they were designed to support to such an extent that by about 1850 atomic theories were virtually abandoned.

Though the ultimate failure of Dalton's theory was due to its inability to define the atoms it postulated, nevertheless the theory contained not only the germ of the modern theory of the atom but indeed foreshadowed that atoms have definite structural parts, and it is remarkable that this inference from the theory should have remained unrecognised for three-quarters of a century, and particularly after the development of the theory of chemical valency from 1852 onwards. A single example is sufficient to illustrate the point. The element manganese forms the following oxides, manganous oxide, manganic oxide, manganous anhydride, manganic anhydride, and permanganic anhydride, in which 100 parts by weight of manganese are combined with 29,  $43\frac{1}{2}$ , 58, 87, and  $101\frac{1}{2}$  parts by weight of oxygen respectively. These weights of oxygen are the simple multiples, 2, 3, 4, 6, and 7, of the common factor  $14\frac{1}{2}$ . Assuming, as Dalton would have assumed, that the first oxide contains one atom of manganese, these oxides would have the formulæ  $\text{MnO}_2$ ,  $\text{MnO}_3$ ,  $\text{MnO}_4$ ,  $\text{MnO}_6$ , and  $\text{MnO}_7$ , identical with the modern formulæ if "O" be taken as a half-atom of oxygen, i.e. a hydrogen equivalent of oxygen. The multiples express precisely the various valencies or combining capacities of the manganese atom measured in terms of atoms of hydrogen or their equivalent, and are unequivocal evidence of the active participation of 2, 3, 4, 6, and 7 of the manganese electrons in binding oxygen atoms. It thus occurs that Dalton's atomic theory, defective though it proved, presaged the ultimate structure of the real atoms it failed to substantiate.

## CHAPTER II

### ATOMS AND MOLECULES

If all atoms have equal combining capacities, measured in terms of atoms of any element taken as a standard, atomic weights and equivalent (combining) weights are identical; but if atoms have different combining capacities, atomic weights can not be determined solely from considerations of equivalent weights. The cardinal defect of Dalton's atomic theory was its failure to provide any means of ascertaining the combining capacities of different atoms. Dalton assumed that the combining capacities of hydrogen, carbon, nitrogen, and oxygen were identical, and that the composition of the ultimate particles of hydrogen, ethylene, ammonia, water, carbonic oxide, and nitric oxide was correctly expressed by the formulæ  $H$ ,  $CH$ ,  $NH$ ,  $OH$ ,  $CO$ , and  $NO$ , whereas they are in fact  $H_2$ ,  $C_2H_4$ ,  $NH_3$ ,  $H_2O$ ,  $CO$ , and  $NO$ , respectively. A decision, as to which of these two series of formulæ is correct, can however readily be made, if the relative weights of the particles and the formula of any one are known. General agreement, as to the composition of the hydrogen particle or molecule, and as to methods for determining the molecular weights of elementary and compound substances, was not reached for over half a century after Dalton's theory was put forward, but this half-century of confusion sufficed to elucidate that atoms have a definite numerical valency, saturation capacity or combining power measured in terms of hydrogen atoms or their equivalent.

In 1805, Gay-Lussac and Humboldt<sup>1</sup> discovered that oxygen and hydrogen combine to form water in the proportion of two of hydrogen to one of oxygen by volume, and in 1808 Gay-Lussac,<sup>2</sup> as the result of further experiments, put forward the **Law of Simple Multiple Proportions by Volume**, which, in modern terms, states that the **several gaseous volumes, measured under standard condi-**

<sup>1</sup> *Journ Phys*, 1805, 60, 129

<sup>2</sup> *Mém Soc Arcueil*, 1809, 2, 207.

tions, of the substances taking part in a chemical change and the total change in volumes, if any, are small integral multiples either of the smallest or of a common factor of these volumes. This law, usually referred to as **Gay-Lussac's Law** or the **Law of Gaseous Volumes**, was strongly opposed by Dalton in 1810, who imagined it was unconfirmable with his atomic theory. Dalton, however, admitted that the law and the atomic theory were compatible, if "*all elastic fluids (gases) have the same number of atoms in the same volume,*" but regarded such a hypothesis as untenable.

The hypothesis abandoned by Dalton was again propounded in 1811 by Avogadro,<sup>1</sup> who showed clearly that Gay-Lussac's Law was thereby readily explicable. **Avogadro's Hypothesis** states that equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of independent particles (molecules). He inferred from the hypothesis that the ratio of the masses of equal volumes of gases is the ratio of the masses of their molecules, or, in other words, that the ratio of vapour densities is the ratio of molecular weights. He further showed that, by means of the hypothesis, Dalton's arbitrary suppositions as to the relative number of atoms in compounds could be rectified or confirmed, and that the so-called atoms of hydrogen, nitrogen, and oxygen must each consist of two half-molecules. Avogadro's argument was that, as the volume of gaseous water formed by combining two volumes of hydrogen with one volume of oxygen was double that of the oxygen, the molecule of oxygen must be double. Similarly, he argued that, as the volume of ammonia was double that of the nitrogen from which it could be formed, the nitrogen molecule must be double, and, further, that, as three volumes of hydrogen yield only two volumes of ammonia, the molecule of hydrogen must be double, i.e. that six half-molecules of hydrogen must have been present in the original three

<sup>1</sup> *Journ Phys*, 1811, 73, 58

molecules. The importance of Avogadro's hypothesis was, however, not realised by chemists, and for the next forty-nine years no certain means existed of determining atomic weights.

Ampère in 1814<sup>1</sup> revived Avogadro's hypothesis, but failed to make it acceptable. A similar fate befell Dumas' attempts<sup>2</sup> to establish a system of atomic weights based on determinations of vapour densities.

In 1819, Dulong and Petit, as a result of investigations of the relations between atomic weights and physical properties, proposed<sup>3</sup> the **Law of Atomic Heat**, which states that the heat required to raise the temperature of a weight of any element, equal to the atomic weight in grams, through 1° C. is constant for all elements, or that the atomic heats of different elements are equal. This law is, however, only approximately true, the constant (6.4 calories) varying for different elements from less than 2 to more than 9 calories. It is available, in the absence of means of determining molecular weights, for fixing atomic weights, and serves as a useful check on atomic weight data. The investigations of Neumann in 1831, and of Regnault in 1841, enabled Joule in 1844 to propose the **Law of Molecular Heat**,<sup>4</sup> which states that the atomic heats of elements are unchanged in their compounds. The exceptions to the heat laws are not only numerous but very marked, discrepant atomic heats, for example, being almost invariably low. It has been frequently suggested that the atomic heats of the discrepant elements are more closely in agreement with the law at very high temperatures, the atomic heat of carbon, for example, increasing from 1.8 at 20° to 6.0 at about 2000°. This suggestion is invalidated by the fact that nearly all elements having normal atomic heats, i.e. about 6.0, have atomic heats as high as 9 to 10 at the temperature at which carbon has 6.0.

<sup>1</sup> *Ann Chim Phys*, 1814, [1], 90, 13

<sup>2</sup> *Ibid*, 1826, [2], 83, 337, and 1837, [2], 50, 170

<sup>3</sup> *Ibid*, 1819, [2], 19, 350.

<sup>4</sup> *Phil Mag*, 1844, [3], 25, 334

Moreover, as all specific heats tend to zero as zero absolute temperature is approached, atomic heats also tend to zero. The fact is that atomic heats are not constant, but that the value 6.4 calories is close to the atomic heats of many elements.

Atomic weights are occasionally determinable on analogies inferred from crystalline structure. In 1820, Mitscherlich proposed the **Law of Isomorphism**, which states that "*the same number of atoms combined in the same manner produce the same crystalline form; the crystalline form is independent of the chemical nature of the atoms, and is determined solely by their number and mode of combination.*" If this law were rigorously true it would be of service in determining the combining capacity or valency of elementary atoms by analogy with similar and isomorphous compounds containing elements of known valency. The law is, however, of very limited application, as the number of exceptions to it are numerous, and as no such phenomenon as exact isomorphism exists even in the case of compounds of elements chemically most closely related, largely due to the non-identity of atomic volumes of any atoms.

Berzelius, who determined the atomic weights of almost the whole of the elements known in his day and the exact composition of the majority of their compounds, was guided, in his decisions as to the numerical relation between equivalent weight and atomic weight, by general considerations based on the well-ascertained reactivities of similar elements in analogous compounds, by Gay-Lussac's law of gaseous volumes in so far as he applied Avogadro's hypothesis to elementary but not to compound gases and vapours, by Dulong and Petit's law of atomic heat, and by Mitscherlich's law of isomorphism. That his atomic weights were frequently amended, by multiples or sub-multiples, and were finally often in error, is to be attributed more to his failure to accept Avogadro's hypothesis for compounds as well as for elements than to the inadequacy of contemporary knowledge. This failure undoubtedly

held back the development of chemistry for at least a generation, as is evident from the fact that, within ten years of the regularising of atomic weights consequent on Cannizzaro's revival and the immediate general acceptance of Avogadro's hypothesis, the obscure facts of valency were disentangled and the periodic classification propounded.

In 1858, Cannizzaro published his *Sketch of a Course of Chemical Philosophy*,<sup>1</sup> by which he firmly established Avogadro's hypothesis and showed that all the known physical and chemical facts as to gaseous bodies confirmed its validity, and that the distinction between atoms and molecules reconciled all the contradictory experimental results accumulated in the preceding half century. Cannizzaro attempted to combine the laws of simple multiple proportions by weight and by volume into one law, that the various weights of the same element contained in equal volumes either of the free element or of its compounds are all whole multiples of one and the same weight, that of the atom. This, however, is not a law but merely a definition of atomic weight, and quite overlooks the important point in Dalton's law of simple multiple proportions, in that the latter deals with the multiples of a weight which is frequently *less* than the atomic weight, and always less than the atomic weight in the cases of elements having combining capacity for hydrogen atoms, i.e. valency, greater than unity. Cannizzaro emphasised that what enters into chemical reactions is the half-molecule of hydrogen, which is "*indivisible, at least in the sphere of chemical actions actually known,*" and deliberately left open the question as to whether or not it was physically possible to divide atoms further, a significant disclaimer in view of modern theories of the many-electroned atom and its composite nucleus.

It is a common delusion of writers in the journals of popular science no less than in the daily press that the discovery of the mobile electron and the disintegrable atomic nucleus destroyed the foundations of chemistry, a science

<sup>1</sup> *Il Nuovo Cimento*, 1858, 7, 321, *Alcemic Club Reprint*, No 16

of indivisible atoms. This delusion has its origin in a misapprehension of what chemists mean by an atom. The integrity of the chemical atom has never been so certain as since it was proved to be physically divisible, and, even had the atom been proved in physics to have no real existence whatever, the atom of chemistry would remain, for it is the name by which one of the real weight relations between different kinds of matter is experimentally identifiable. The precise meaning attached in chemistry to the term atom is involved in the definition, that **the Atomic Weight of an element is a number equal to thirty-two times the ratio of the smallest weight of it, ever found in a gaseous volume of it or of any of its compounds, to the weight of an equal gaseous volume of oxygen at the same temperature and pressure.** This number is very nearly identical with twice the corresponding ratio referred to hydrogen as the standard. From this definition it is obvious that an atomic weight is an experimentally determinable number which is totally independent of the reality of the existence of physical atoms. Atomic weights are not measureable in grams or pounds, but are mere numbers, expressing the ratio of one weight to a specifically selected weight of an arbitrary standard. Cannizzaro chose hydrogen as the standard element, but, for reasons of accessibility of measurement, the modern standard element is oxygen.

The definition of atomic weight is so framed that even the atomic weight of the standard element can be experimentally determined. The weights of equal volumes of gaseous water and gaseous oxygen are in the ratio 9 to 16, and 9 parts by weight of water contain 8 parts by weight of oxygen, and, by definition, the atomic weight of oxygen in water is 32 times the ratio  $\frac{9}{16}$ , i.e. 16. As this is the *smallest* atomic weight ever found in an oxygen compound, the atomic weight of oxygen is 16. The atomic weight of hydrogen in water is 32 times the ratio  $\frac{1}{16}$ , i.e. 2, deduced from the fact that 1 part by weight of hydrogen is contained in 9 parts by weight of water, and 16 parts by weight of

gaseous oxygen are contained in a volume equal to that of 9 parts by weight of gaseous water. This atomic weight of hydrogen is *not the real atomic weight*, for compounds of hydrogen are known, from which an atomic weight about half of the foregoing is obtained, 1.008 to be exact.

As equal gaseous volumes of oxygen and water have weights in the ratio of 9 to 16, and water contains eight-ninths of its weight of oxygen, the ratio of the oxygen in water to the oxygen in gaseous oxygen is 1 to 2 by weight. By Avogadro's hypothesis the ratio of the weights of equal volumes of gases is the ratio of the weights of the particles of which the gases are composed, i.e. the weights of the molecules. As the weight of oxygen in gaseous oxygen is twice that in an equal gaseous volume of water, the molecular weight of gaseous oxygen is 32, i.e. twice the atomic weight of oxygen deduced from the composition of water. In general the **Molecular Weight of an element or compound is a number equal to thirty-two times the ratio of the weight of a gaseous volume of the element or compound to the weight of an equal volume of oxygen at the same temperature and pressure.** Obviously, if the molecular weight be so defined, the **Atomic Weight of an element is the least weight of it ever found in the molecular weight of it or of any of its compounds.** In the case of many elements, the molecular weight is not identical with the atomic weight, but a simple multiple of it. This multiple, known by the term "**Atomicity**," defines the **number of atoms in the elementary molecule.** Originally this term was applied to the combining capacity of an element measured in atoms of hydrogen, but the term valency is now used for combining capacity, and atomicity applied only to the composition of the molecules of elements.

A definition, common in text-books of chemistry, is that the atom or the molecule represents the least weight of a substance that can take part in a chemical change. This definition is untrue for many reasons. The "*least weight*" must be that of the *real* atom, which, in the case of hydro-

gen, is so small that about six hundred thousand million billions are required to weigh one gram. Apart from absolute weights, the least weight of an element that can be discerned in a chemical change is not necessarily the molecular weight or the atomic weight, but usually a smaller weight termed the equivalent weight, and equal to the atomic weight and molecular weight only in the case of the alkali metals, which have invariable unit valency. **The Equivalent Weight of an element or compound is defined as a number equal to eight times the ratio of the weight of it to the weight of oxygen with which it combines or which it can displace from combination.** As the ratio of the weights of hydrogen and oxygen in water is one-eighth, one equivalent weight of hydrogen is practically equal to unity, hence is derived an alternative definition, that **the equivalent weight of a substance is the weight that combines with or displaces from combination one part by weight of hydrogen.** The atomic weight of hydrogen being very nearly unity, the equivalent weight represents the weight that combines with or displaces from combination one atom of hydrogen, and the atomic weight of oxygen being 16 the equivalent weight of oxygen is half an atom, i.e. 8. The equivalent weight of water,  $\text{H}_2\text{O}$ , is the half-molecule of weight 9. The equivalent weight of orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , is a third of the molecule, of sulphuric acid,  $\text{H}_2\text{SO}_4$ , a half-molecule, and of hydrochloric acid,  $\text{HCl}$ , a whole molecule. In the case of acids **the ratio of the molecular weight to the equivalent weight is termed the "Basicity" of the acid**, mono-basic, dibasic, tribasic, and tetrabasic acids containing one, two, three, and four atoms of hydrogen, respectively, in the molecular weight. The equivalent weight of the base caustic soda,  $\text{NaOH}$ , is the whole molecule for it combines with one molecule of a monobasic acid, of the base lime,  $\text{CaO}$ , the half-molecule, for it combines with one molecule of a dibasic acid, and of the base alumina,  $\text{Al}(\text{OH})_3$ , one-third of the molecule, for it combines with one molecule

of a tribasic acid. In the case of bases, the ratio of the molecular weight to the equivalent weight is termed the "Acidity" of the base, and the molecules of mono-acidic, di-acidic, tri-acidic, and tetra-acidic bases respectively combine with one, two, three, and four atoms of hydrogen of acids.

The equivalent weight in the case of an element is not necessarily a constant, manganese, for example, forming at least five different compounds with oxygen. The various equivalent weights in these oxides range from 27.5 to 7.85. The oxide with the *smallest* equivalent dissolves in water to form an acid in which the ratio of hydrogen to manganese is 1 to 55, and as the acid cannot contain *less* than an *atom* each of hydrogen and manganese, the atomic weight of the latter cannot be *greater* than 55. Only a knowledge of the molecular weights of all manganese compounds can suffice to determine the actual atomic weight. The molecular weights of many compounds cannot be obtained, however, owing to the impossibility of obtaining them in the gaseous condition.

Investigation of the properties of solutions of substances in liquids has disclosed the fact that an internal pressure, called the **Osmotic Pressure**, is set up in dilute solutions, such that this pressure is **approximately equal to that exertable by the same weight of the dissolved substance if it existed as a gas and occupied the same volume as that of the solution**. Comparison of the osmotic pressures of different substances enables relative molecular weights to be determined by reference to properties of the solutions which are dependent on the magnitudes of the osmotic pressures. Such properties are lowering of the vapour pressure of the solvent, elevation of its boiling point, depression of its freezing point, and lowering of its solubility for other substances. Determinations of molecular weights based on the properties of solutions are seldom more than approximately exact, but the results usually serve to decide which multiple of the equivalent weight is

the true molecular weight, and hence enable atomic weights to be fixed in cases where the vapour density method is inapplicable

It has often been stated that atomic weights are matters of essentially minor importance, and that past generations of chemists have wasted incalculably valuable time, energy, and skill, in the determination of a mere number, a relative weight, which, as some modern physicists have declared, is not even a characteristic property of any sort of matter. Such statements can be viewed by chemists only as pathetic confessions of ignorance. The weight properties of matter are in fact almost the only properties of matter that have enabled the innermost secrets of nature to be unveiled. The ratio of atomic weight to equivalent weight is the sole determinant of the combining capacity or valency of atoms, and the whole of modern knowledge of the complex structures of organic and inorganic chemistry rests and abides in valency. Without a knowledge of atomic weights and valency the classification of the elements in terms of periodic properties is inconceivable, and without the periodic classification there could have been no hope of the explanation of radioactivity, or of the arrangement of numerous electrons into the ordered systems of present-day physical and chemical theories of atomic structure.

The two factors which are stated to render ordinary atomic weights unreal, are the existence of **Isotopes (isomeric atoms identical in all properties except mass)** and the circumstance of the variation of all mass with velocity. Whatever the facts may be as to the existence of isotopes, there is no doubt that throughout nature atomic weights are constant, and isotopic atoms must therefore be present in a constant proportion in any directly weighable amount of any element. Consequently atomic weights are real if only real averages, and their validity in chemistry is independent of the existence of isotopes. The minute variation of mass with velocity is based on known variation with velocity in the value of the ratio of electric charge to mass

Obviously one of the factors of the ratio must be variable, but it is a mere hypothesis that the variable factor is mass—it may in fact be electric charge, and it is certain that the differences in the values of the unit electric charge, that of the ion or electron, are greater than the possible differences due to variation with velocity, so that the hypothesis of the constancy of electric charge with variable velocity has no evidence to support it, and, it may be argued, is not a fundamentally necessary hypothesis for the explanation of the variation of the ratio of charge to mass. Even should the variation in the charge to mass ratio be ultimately demonstrated to be wholly due to variation in mass, this variation is practically zero at all velocities much less than that of light, and is extraordinarily minute even with attainable velocities comparable with that of light. Any possible variations in mass that could occur in any chemical reaction, conducted on substances at any practicable velocity, would lie far outside any hope of detection by any chemical methods of direct weighing, and consequently the variation in mass with velocity has no real bearing on the chemical validity of atomic weights.

## CHAPTER III

### VALENCY

THE mechanism of chemical combination is the root problem of chemistry, and theories regarding it were propounded even prior to the chemical theory of atoms. In 1787, Moivreau suggested that compounds consisted of oxygen combined with a base or radical,<sup>1</sup> and Lavoisier<sup>2</sup> regarded all compounds as oxides, and suggested that inorganic bodies were oxides of simple substances and organic bodies oxides of complexes or *radicals*. Lavoisier's theory was essentially *dualistic*, for he divided the oxides into two contrasting classes, those that were derived from acidic and those from salifiable radicals or bases. To Lavoisier, all radicals were bases, but the term "bases" was later restricted to the oxides of metals, acid radicals being those whose oxides gave rise to acids.

In 1815, Gay-Lussac<sup>3</sup> showed that cyanogen was a never-varying constituent group or radical of a series of compounds, and was chemically equivalent to the simple acidic radicals (elements).

In 1820, Dalton discovered a hydrocarbon in oil-gas having the same composition as ethylene, and it was later suggested that it consisted of two ethylene particles. The composition of this hydrocarbon, now known as butylene, was confirmed by Faraday in 1825,<sup>4</sup> who showed that its vapour density was twice that of ethylene, and at the same time announced the discovery of another hydrocarbon, benzene. Faraday called attention to a number of existing cases of substances having the same composition but different properties, and cited Liebig's discovery of 1823 that the latter's silver fulminate and Wöhler's silver cyanate had the same composition,<sup>5</sup> and Gay-Lussac's suggestion

<sup>1</sup> Lavoisier, Moivreau, and Fourcroy, *Méthode de Nomenclature*, 1787

<sup>2</sup> *Traité élémentaire de Chimie*, 1789 and 1793

<sup>3</sup> *Ann Chim Phys*, 1815, [1], 95, 136

<sup>4</sup> *Phil Trans Roy Soc*, 1825, 461.

<sup>5</sup> Liebig, *Gilbert's Ann*, 1823, 75, 393, *Ann Chim Phys*, 1823, [2], 24, 294, and Gay-Lussac and Liebig, *ibid.*, 1824, [2], 25, 285

that the difference in properties of substances with the same composition must be due to differences in the arrangements of the same atoms.

Wöhler's discovery in 1828<sup>1</sup> that the salt, ammonium cyanate, is converted, by simply heating in aqueous solution, into the organic substance, urea, having the same qualitative and quantitative composition, lent additional weight to Gay-Lussac's suggestion. In 1831, Berzelius<sup>2</sup> showed that racemic acid, discovered in "tartar" (winelees residues) by Gay-Lussac, was identical in chemical composition and many chemical properties with ordinary tartaric acid, but differed from it in solubility and in the crystalline form of its salts. To express this difference in properties of substances with identical composition, Berzelius proposed the term "**Isomerism.**" He further indicated that Mitscherlich's law of isomorphism must be amended in a new direction, in that the same atoms may be arranged in chemically very similar substances so as to produce different crystalline forms. The demonstration of the existence of isomeric bodies involved the recognition of the fact that the atoms in a compound were *not* combined together "*each to all and all to each,*" but that specific atoms must be differently combined together. From this time chemistry acquired a new outlook, and the important problem of the science became the determination of the details of the combination between atoms. In the subsequent theories of radicals, nuclei, substitutions, and types, chemical conceptions of the molecule with definite structure and of the atom with delimited and directional combining capacity slowly clarified and finally crystallised into the modern theories of molecular structure and atomic valency.

In 1827, Dumas and Boullay<sup>3</sup> propounded the theory that ether and the simple derivatives of ethylene all

<sup>1</sup> *Pogg Ann*, 1828, 12, 258

<sup>2</sup> *Fabresber*, 1832, 11, 44, and 12, 63

<sup>3</sup> *Ann Chim Phys*, 1828, [2], 36, 294, and 1828, [2], 37, 15

contained the ethylene group,  $C_4H_8$ , for which Berzelius proposed the name etherin. Liebig, however, adopting the dualistic view, regarded ether as the oxide of the radical,  $C_4H_{10}$ , which he called etheryl or ethyl. In 1832, Wöhler and Liebig<sup>1</sup> published their researches on the "*Radical of Benzoic Acid*," and described a series of closely related, interconvertible compounds all containing the radical benzoyl.

In 1834, Dumas, as the result of his researches on the action of chlorine on alcohol,<sup>2</sup> put forward his "**Substitution Theory**," in which he postulated that hydrogen in organic compounds could be replaced atom for atom by chlorine, bromine, and iodine, and the equivalent of oxygen, without very material alteration in the nature of the resultant products. This theory was expanded by Laurent<sup>3</sup> into the "**Nucleus Theory**," in which the carbon atoms in compounds were regarded as forming an invariable nucleus of definite shape, the various atoms round the nucleus being substitutable, equivalent for equivalent, without material change in nature of the compounds.

In 1837, Liebig,<sup>4</sup> and Dumas and Liebig,<sup>5</sup> put forward their "**Theory of Radicals**," now called the "**Older Theory of Radicals**," in which complex groups of atoms or radicals were assumed to exist in organic compounds, and to be transferable unchanged from compound to compound like the elementary atoms of inorganic compounds. Gerhardt, however, rejected the theory of unchangeable radicals and proposed a "**Theory of Residues**"<sup>6</sup> in which he regarded an organic molecule as a single structure, not a binary system of radicals. To Gerhardt, radicals were merely the portions, residues, that took no part in a particular chemical reaction, and appeared as independent

<sup>1</sup> *Ann*, 1832, 3, 249

<sup>2</sup> *Ann. Chim. Phys.*, 1834, [2], 56, 113 and 140

<sup>3</sup> *Ibid.*, 1835, [2], 60, 220, 1836, [2], 61, 125, and 63, 27, 42, 207, and 377

<sup>4</sup> *Ann*, 1838, 25, 3

<sup>5</sup> *Compt. rend.*, 1837, 5, 567, and *J. prakt. Chem.*, 1838, 14, 298

<sup>6</sup> *Ann. Chim. Phys.*, 1839, [2], 72, 184

portions of molecules only when displaced in a reaction by combination between the reacting portions of molecules, such residues or unreactive remnants then joining together to form a copulated or conjugated compound.

In 1840, Dumas incorporated his theories of radicals and substitutions, together with portions of Laurent's nucleus theory and Gerhardt's theory of residues, into a comprehensive "Theory of Types"<sup>1</sup> now referred to as the "Older Theory of Types." Dumas regarded substances, with similar properties and analogous composition, as belonging to one *chemical type*, for example, acetic acid and trichloroacetic acid; and substances, with different properties but simply derivable from one another, as belonging to the same *mechanical* or *molecular type*, for example, alcohol and acetic acid. He specially emphasised the importance of the arrangements of atoms and radicals in the molecule as determinants of chemical properties.

Berzelius, realising the incompatibility of his dualistic theory of electro-chemical combination<sup>2</sup> with the substitution theory, attempted to explain the facts of equivalent substitution by postulating imaginary radicals, trichloroacetic acid, for example, being regarded as a copulated compound of carbon chloride,  $C_2Cl_6$ , and the carbon oxide,  $C_2O_3$  (oxalic acid), together with water. This explanation broke down when it was shown that on reduction trichloroacetic acid yielded only hydrochloric and acetic acids and no oxalic acid, and, though Berzelius was unconvinced and continued to oppose the type theory till his death in 1848, his dualistic theory, once the most important and widely accepted in Europe, was almost completely abandoned by 1840.

In 1808, Thomson (T.) had shown that oxalic acid combined with both potash and strontia to yield two series of compounds in which one contained twice as much of the

<sup>1</sup> *Ann Chim Phys*, 1840, [2], 73, 73, 113, and 74, 5.

<sup>2</sup> See Chap IV, p. 48

bases as the other,<sup>1</sup> and in the same year Wollaston<sup>2</sup> showed that carbonic and sulphuric acids had saturating capacities for bases similar to oxalic acid. In 1833, Graham<sup>3</sup> proved that phosphoric acid,  $\text{PO}_5$ , unites with one, two, or three equivalents of water,  $\text{OH}$ , to form separate acids,  $\text{HPO}_6$ ,  $\text{H}_2\text{PO}_7$ , and  $\text{H}_3\text{PO}_8$ , ( $\text{HPO}_3$ ,  $\text{H}_4\text{P}_2\text{O}_7$ , and  $\text{H}_3\text{PO}_4$ , in modern formulæ), characterised by their ability to combine with one, two, or three equivalents, respectively, of bases. It followed, consequently, that equal numbers of molecules of acids (acidic oxides) and bases (basic oxides) did not necessarily neutralise one another. This controverted the rule set up by Berzelius that the molecular weight of an acid was equal to the relative weight required to neutralise the equivalent weight of a base. In 1838, Liebig published his "**Theory of Polybasic Acids**"<sup>4</sup> and showed clearly that, before the molecular weight of an acid could be determined, it was necessary to know its **saturation capacity for bases**, i.e. its **basicity**. Liebig's interpretation that **acids are salts of hydrogen** (based on an earlier suggestion of Davy, who argued that hydrochloric acid was an acid though it contained no oxygen), involved that the hydrogen atoms, in a radical combined with oxygen, were differentiable into two classes according as the hydrogen atoms were or were not replaceable by metals to give salts, thus elucidating part of the structure of carbon-hydrogen radicals. Gerhardt incorporated Liebig's theory of basicity into his "**Theory of Residues**" (see p 36) and showed that the basicity of a copulated or conjugated compound was always one less than that of its constituents, *non*-basic benzene, for example, and *di*basic sulphuric acid forming *mono*basic benzene sulphonc acid.

In 1844, Mitscherlich showed that, though solutions of salts of ordinary tartaric acid rotated the plane of polarisation of light whereas those of racemic or paratartaric acid

<sup>1</sup> Thomson, *Phil. Trans. Roy. Soc.*, 1808, **98**, 63

<sup>2</sup> *Ibid.*, **98**, 96.

<sup>3</sup> *Ibid.*, 1833, **123**, 253

<sup>4</sup> *Ann.*, 1838, **26**, 113.

were optically inactive, yet the salts exhibited the same crystalline form. Pasteur, in 1848, however, found on further examination, that crystals of salts of racemic acid were not truly uniform but were composed of two sorts, one identical in all chemical and optical properties with the salts of ordinary tartaric acid, the other being also identical except that solutions rotated the plane of polarisation of light in the reverse direction. This opposition in the optical properties was shown to be parallel with the development on one of the sorts of crystals of small facets (hemihedral facets) related to the corresponding facets on the other sort as object to non-superposable mirror-image.<sup>1</sup> This discovery led later to the theory of the *tetrahedral* carbon atom and the asymmetry of organic molecules, and, in the hands of Werner, led to the brilliant elucidation of the constitution of complex inorganic molecules, and, inferentially, to a decisive knowledge of the exterior structure of the atoms of many elements.

In 1849, Wurtz discovered the organic amines or substituted ammonias,<sup>2</sup> and proposed that these bodies all be referred to the general type, ammonia,  $\text{NH}_3$ , by replacement of one or more hydrogen atoms by radicals. Wurtz's suggestion of the ammonia type was adopted by Hofmann,<sup>3</sup> who had prepared a similar series of substituted ammonias.

In 1850, Williamson, as a result of his researches on "*Etherification*,"<sup>4</sup> suggested that all compounds could be referred to the **water type**,  $\text{H}_2\text{O}$ , or to the type of condensed molecules of water ( $\text{H}_2\text{O}$ )<sub>n</sub>.

In 1851, Kolbe put forward his "**New Theory of Radicals**," supported by his work on the free radicals obtained by the electrolysis of organic acids, and by his joint researches with Frankland on the organometallic bodies, which contained readily identifiable hydrocarbon

<sup>1</sup> *Compt rend*, 1848, 26, 535, and 27, 101, and 1849, 28, 223

<sup>2</sup> *Ibid*, 1849, 28, 223, and *Ann Chim Phys*, 1850, [3], 30, 498.

<sup>3</sup> *Ann*, 1850, 73, 91, 74, 174, and 1851, 79, 16

<sup>4</sup> *Brit Assoc Rep*, 1850, 2, 65, *Phil Mag*, 1850, 37, 350, *Proc Roy Instn*, 1851-1854, 1, 90, and 239, *J Chem Soc*, 1852, 4, 229, 239, and 350

radicals directly combined with metals. Kolbe and Frankland regarded numerous organic substances simply as derivatives of inorganic substances, from which they could often be obtained by simple substitution processes, and suggested that all organic bodies could be regarded as derived from carbonic acid<sup>1</sup>

In 1852, Frankland (E.) published his classical research on *A New Series of Organic Compounds containing Metals*,<sup>2</sup> and showed that the power of metals to combine was reduced by copulation with organic radicals in organo-metallic compounds, in the same way that acids are reduced in basicity by copulation (Gerhardt's Theory of Residues, p. 38). This reduction in power of combination on copulation was shown by Frankland to vary directly with the number of radicals copulated to the metallic atom in the same way and to the same extent as partial combination with oxygen reduced the power of combination with other atoms, and he therefore regarded combination with radicals as being in no way different from ordinary inorganic combination. The views put forward by Frankland as to the definite combining power of individual atoms constituted the first direct explanation of Dalton's law of simple multiple proportions and Liebig's and Gerhardt's rules as to the basicity of acids and radicals, and represent the first definite steps towards the establishment of the theory of **Valency**. The fact that Frankland regarded the oxygen atom, in Gmelin's notation, as equivalent to an atom of hydrogen, in no way detracts from his recognition of the definite combining capacity of atoms or valency. The prevailing confusion in atomic weights, however, obscured the importance of his contribution to chemical theory. Nevertheless, his method of formulation of combining capacity is not merely strictly admissible but necessary, for valency is determinable not in terms of any atoms but in terms of the equivalents of atoms,

<sup>1</sup> *Ueber die chemische Konstitution und Natur der organischen Radikale*, 1851, *Ann.*, 1849, 69, 257, 71, 171, 1850, 75, 211, 76, 1, 1857, 101, 257, and 1860, 113, 293

<sup>2</sup> *Phil Trans Roy Soc*, 1852, 142, 417.

i.e. in terms of hydrogen atoms with unit combining capacity

In 1853, Gerhardt put forward his "Theory of Simple Types"<sup>1</sup> in which he included Wurtz's ammonia type and Williamson's water type in a scheme of formulation of organic compounds, such that all were regarded as derived from the four simple inorganic types, hydrogen,  $H_2$ , hydrochloric acid,  $HCl$ , water,  $H_2O$ , and ammonia,  $NH_3$ . He further classified radicals, according to their "atomicity," or their capability of replacing one, two, or three atoms of hydrogen in the type from which their compounds were derived. Wurtz<sup>2</sup> similarly classified radicals according to their "basicity," or capacity to replace hydrogen atoms in compounds. In the same year Odling introduced the system of placing dashes as an index to the atom symbol to convey the numerical value of the element in replacing hydrogen atoms, and indicated his agreement with Frankland as to the definite but, within limits, variable combining capacity of some elements<sup>3</sup>

In 1857, Kekulé proposed the addition of a new type, methane,  $CH_4$ , to Gerhardt's types, and suggested that the  $HCl$  type was redundant, being a variant of the  $H_2$  type<sup>4</sup>. Kekulé clearly recognised that the carbon atom was equivalent to four hydrogen atoms, thus clarifying Kolbe's suggestion that all organic compounds could be regarded as derived from carbonic acid,  $CO_2$ . He further showed that Gerhardt's residues were radicals unattacked in chemical reactions, and elaborated Gerhardt's suggestion of mixed types, i.e. compounds derived from more than one fundamental type according to the atom selected as the type nucleus.

In 1858, Cannizzaro published his celebrated *Sketch of a Course of Chemical Philosophy*,<sup>5</sup> by which he not merely

<sup>1</sup> *Traité de Chimie Organique*, Paris, 1853, I, 132, IV, 589 and 600

<sup>2</sup> *The Atomic Theory*, 1855, p. 200

<sup>3</sup> *J. Chem. Soc.*, 1855, 7, 1

<sup>4</sup> *Ann.*, 1857, 101, 200, 104, 129, and 133

<sup>5</sup> *Il Nuovo Cimento*, 1858, 7, 321.

established Avogadro's hypothesis and the real distinction between equivalent, atomic, and molecular weights, but demonstrated the existence of "polyatomic" radicals among the simple atoms, thus extending Gerhardt's conception of "atomicity" or saturation capacity from organic to inorganic chemistry. He showed that hydrogen, potassium, sodium, lithium, silver, cuprous, and mercurous atoms were "monoatomic" (univalent) electro-positive radicals, that the halogen elements, chlorine, bromine, and iodine, were monoatomic electro-negative radicals, that zinc, lead, magnesium, calcium, etc., were "diatomic" (bivalent) electro-positive radicals, and oxygen, sulphur, selenium, and tellurium were diatomic electro-negative radicals, and, further, that atoms existed that were equivalent to three or more atoms of hydrogen or chlorine.

In the same year, Kekulé brought forward, probably independently, a theory of "polyatomicity,"<sup>1</sup> practically identical with that of Cannizzaro, though there is little doubt that Cannizzaro's views had been developed and imparted to his students many years before Kekulé's ideas had crystallised, as is evident from Kekulé's ambiguous paper on the methane type of the previous year. Kekulé disagreed with Frankland's views as to variable "atomicity," and held that the combining capacity of an element was a fixed property of the atom, as exemplified by the constant "atomicity" of carbon in organic compounds. Both views were right, for it is now clearly recognised that some elements have fixed and some elements variable "atomicity" or valency.

Almost simultaneously with the publication of Kekulé's theory of "polyatomicity," Couper<sup>2</sup> published a paper in which he deduced formulæ for compounds based on what he called the "elective affinities" and the "affinity of degree" of atoms, identical with Cannizzaro's and Kekulé's

<sup>1</sup> *Ann*, 1858, 106, 129

<sup>2</sup> *Phil Mag*, 1858, [4], 16, 104, and *Compt rend*, 1858, 46, 1157

"atomicity" (valency). Both Couper and Kekulé recognised that in organic compounds the carbon atoms must be regarded as combining among themselves so that only part of their affinity or combining capacity was available for binding other atoms. Couper, to symbolise the combination between atoms, introduced the method of joining the atom symbols by means of hyphens or dots, and this method was amplified by Crum Brown,<sup>1</sup> who re-introduced Dalton's system of enclosing the symbol in a circle, Couper's hyphens becoming radiating lines equal in number to the combining capacity. Frankland, in 1866, by omitting Crum Brown's circles, stereotyped the method of formulation now in use<sup>2</sup> and introduced the term "bond" to signify the unit of valency.

Gerhardt had laid it down in his *Traité de Chimie Organique*, Paris, 1853, IV, 561, that "*it is a widely prevalent error to suppose the possibility of representing molecular constitution by means of chemical formulæ, or in other words by the actual arrangement of atoms.*"

The polyatomicity and elective affinity theories of Kekulé and Couper had, however, no other aim than the determination of atomic arrangements. Definiteness was lent to this aim by Butleroff's pronouncement in 1861<sup>3</sup> that the chemical nature of a compound was determined firstly by its qualitative and quantitative composition, and secondly by its chemical "structure," by which he meant the mode of mutual linking of the atoms in the molecule. Practically the whole of research in organic chemistry since that date has been devoted to the determination of the **structural** or **constitutional formulæ** of compounds, by means of which we are to-day enabled to elucidate the nature of the mechanism of atomic linkages and the superficial structure of atoms.

In 1863, Erlenmeyer<sup>4</sup> suggested that the term "*basicity*"

<sup>1</sup> *J Chem Soc*, 1865, 18, 230

<sup>2</sup> *Lecture Notes for Chemical Students*, 1866

<sup>3</sup> *Zeit Chem*, 1861, 4, 549

<sup>4</sup> *Ibid*, 1863, 6, 65, 97, and 609

be reserved for the combining capacity of acids, instead for both atoms and acids, and proposed the terms *ein-*, *zwei-*, *drei-*, and *vier-weißig* (= *worth*), to express the numerical value of atomic combining capacity. In 1866 Odling suggested the terms *monad*, *dyad*, *triad*, *tetrad*, etc. and these terms are still in occasional use. Hofmann's book, *Introduction to Modern Chemistry*, published in London in 1865, contributed greatly to the clarification of ideas concerning combining capacity, and he proposed for it the term "*quantivalence*," to indicate its dependence on equivalent weights and its numerical value. This term was shortened to "**valency**" (or "valence") by Wichehauser in 1868,<sup>2</sup> and this term is now in almost universal use. Confusion, however, continues to exist as to the proper prefixes to be used in connexion with valency, both Greek and Latin prefixes being used by different writers. Although, however, valency is definitely of Latin origin (*valens* = *strong*), it is more consistent nomenclature to use the Latin prefixes, and, historically, more accurate, for Hofmann used "*quantivalence*" not "*polyvalency*," when the term originated. The terms **uni-**, **bi-**, **quadri-**, **quinquesexa-**, and **septavalent** are, therefore, to be preferred to *mono-*, *di-*, *tetra-*, *penta-*, *hexa-*, and *heptavalent*, the prefixes *tri-* and *octa-* being the same in both Latin and Greek.

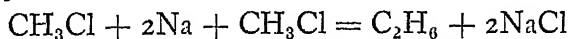
In modern terms **Valency** is defined as the definite limited capacity possessed by an atom for combining with other atoms measured numerically in hydrogen atoms or equivalent atoms or radicals. It is usual to reserve the term "valency" to designate the whole combining capacity of an atom, and to use the term "valence" to specify particular parts of valency, it being thus synonymous with the chemist's use of the term "bond" or "linkage." The "*valency*" of carbon, for example, is four, but two only of the four "*valences*" are apparent in carbon monoxide.

<sup>1</sup> *Watt's Dictionary*, London, 1864

<sup>2</sup> *Ann. Suppl.*, 1868, 6, 257

Precision has been lent to this distinction between valency and valences by the modern numerical identification of valences with *electrons*, valency thus being the number of electrons available or required for combination prior to the fact of combination, and the valences being the individual electrons that actually take part in the combination. For example, hydrogen is univalent, having only one or requiring another electron, but in the molecule of hydrogen two valences exist between the two atoms, owing to the utilisation of both electrons in the combination.

A usual definition of valency is that it is the ratio between the atomic and equivalent weights of an atom. It has been indicated that in complex hydrocarbons, this ratio has not an integral value, the equivalent weight of carbon, for example, in hexane,  $C_6H_{14}$ , being  $5\frac{1}{7}$ , thus involving a valency of  $12 - \frac{32}{7} = 2\frac{1}{7}$  atoms of hydrogen. It is obvious, in fact, that equivalent weights must vary continuously from compound to compound in cases where several similar atoms are combined with each other, their valency, consequently, is not determinable by atoms of other elements. The extent to which the valency of an element is to be regarded as due to combination with other atoms of the same element, may usually be deduced from synthetic or analytical reactions. Ethane, for example, can be synthesised from two molecules of methyl chloride and two atoms of sodium, two molecules of salt being the by-product



If the valency of carbon in methyl chloride is four, due to combination with three atoms of hydrogen and one of chlorine, the valency of carbon in ethane may still be regarded as four by the replacement of a chlorine valence by one valence of another carbon atom, the structure of ethane thus being  $H_3C-CH_3$ . Similar considerations lead to the formula  $H_2C=CH_2$  for ethylene and  $HC\equiv CH$  for acetylene. This conception of *single*, *double*, and *triple*

bonds, and the constant quadrivalency of carbon, led immediately after 1858 to a remarkably rapid development of the theory of the spatial structure of organic molecules and later to the demonstration of the *tetrahedral* distribution in space of the valences of the atoms of carbon, nitrogen<sup>1</sup>, sulphur<sup>2</sup>, selenium<sup>3</sup>, tin<sup>4</sup>, silicon<sup>5</sup>, phosphorus and arsenic<sup>7</sup>.

<sup>1</sup> Le Bel, *Compt. rend.*, 1891, 112, 724, Pope and Peachey, *J. Chem. Soc.* 1899, 75, 1127

<sup>2</sup> Pope and Peachey, *ibid.*, 1900, 77, 1072, Smiles, *ibid.*, 1900, 77, 1174

<sup>3</sup> Pope and Neville, *ibid.*, 1902, 81, 1552.

<sup>4</sup> Pope and Peachey, *Proc. Chem. Soc.*, 1900, 16, 42 and 116

<sup>5</sup> Kipping, *J. Chem. Soc.*, 1907, 91, 209 and 717, 1908, 93, 457

<sup>6</sup> Meisenheimer and Lichtenstadt, *Ber.*, 1911, 44, 356, Kipping and Challenger, *J. Chem. Soc.*, 1911, 99, 626.

<sup>7</sup> Burrows and Turner, *ibid.*, 1921, 119, 426.

## CHAPTER IV

### ELECTRO-CHEMISTRY

IN 1789, Tioostwyk, Deiman, and Cuthbertson, on passing powerful electrostatic charges of electricity through water, discovered that gas was produced which re-formed water on being sparked.<sup>1</sup> Pearson and Cuthbertson, who repeated the experiment in 1797, showed that the gas produced was a mixture of hydrogen and oxygen in the proportions in which the gases were assumed to combine to form water.<sup>2</sup> Nicholson (W.) and Carlisle, by collecting the gas formed at each electrode, showed that hydrogen was evolved at one electrode and oxygen at the other.<sup>3</sup> Ritter, who had for some years been working on the chemical decompositions produced by electricity, in the same year, independently obtained the same results as Nicholson and Carlisle, and came to the conclusion that water united with negative electricity to form oxygen and with positive electricity to form hydrogen, and that electricity took part in all chemical combinations and decompositions.<sup>4</sup>

It had been a common observation that both acids and alkalis as well as oxygen and hydrogen are produced in the electrolysis of water, and in 1806 Davy proved that the acids and alkalis were derived from impurities in the water.<sup>5</sup> In 1803, Berzelius and Hisinger showed that neutral salts in solution in water could be decomposed into acids and alkalis by electrolysis, and in 1807 Davy effected his memorable electrolytic isolation of the alkali metals, potassium and sodium, from fused caustic potash and caustic soda. On this foundation Davy erected his electrical theory of chemical affinity,<sup>6</sup> in which he assumed that bases (metals) are attracted by negative and oxygen by positive electricity. Davy so far developed his electrochemical theory as to

<sup>1</sup> *Journ Phys*, Nov, 1879

<sup>2</sup> *Phil Trans Roy Soc*, 1797, 142.

<sup>3</sup> *Nicholson's Journ.*, 1800, 4, 179

<sup>4</sup> *Voigt's Mag*, 1800, 2, 356, and *Gilbert's Ann*, 1801, 9, 234, and 1802, 10, 282

<sup>5</sup> *Phil Trans. Roy. Soc*, 1807, 1

<sup>6</sup> *Ibid.*, 1808, 1, and 333.

regard all chemical combinations as due to manifestation of electricity between particles, ordinary electrical effects being regarded as the sum of the "particular" effects spread over large masses.

Between 1809 and 1811, Avogadro advanced an electrical chemical theory similar to Davy's, and arranged substances in a series in the order in which they play the part of acid or alkali towards one another, and showed that this series is the same as that in which they are arranged according to their development of positive or negative electricity on mutual contact. He regarded oxygen as being the most electro-negative substance, and ranked other substances according to their "*oxygenicity*" or tendency to play the part of an acid, substances thus ranging from strongly acidic through neutral to strongly alkaline.<sup>1</sup>

In 1812, Berzelius put forward an electrical theory of chemical combination, known as the "**Dualistic Theory**" which dominated the field of chemistry for over quarter a century.<sup>2</sup> Like Davy and Avogadro, Berzelius regarded oxygen as the most electronegative element, but he further assumed that every atom had two electrical poles, one positive and one negative, usually of unequal strength, the atom thus having a predominating polarity. Chemical combination of the first order was that between elementary atoms by a complete or partial neutralisation of opposite electricities, whereas combination of the second order was that between two particles of the first order having unneutralised residues of opposite electricities. Baryta, Ba, for example, was regarded as possessing a residual positive electrification, and sulphuric acid (anhydride),  $\text{SO}_3$ , residual negative electrification, combination between the resulting in completely neutral "heavy spar" (barium sulphate),  $\text{BaSO}_4$  or  $\text{BaO}.\text{SO}_3$ .

Faraday's work on the laws of electrolysis in 1833

<sup>1</sup> *Journ Phys*, 1809, 68, 142, 1810, 69, 1, and 1811, 73, 58

<sup>2</sup> *Schweigger's Journ.*, 1812, 6, 119, *Essay upon the Theory of Chemical Proportions and the Chemical Action of Electricity*, Stockholm, 1814, *Treatise upon Chemistry*, 1817

disclosed that the chemical equivalents of elements are associated with equal quantities of electricity, thus definitely controverting Berzelius' assumption of unequal charges. Dumas' proof in 1834 that electronegative chlorine could replace electropositive hydrogen, equivalent for equivalent, without material change in chemical properties, extended the inapplicability of the dualistic theory from inorganic to organic chemistry, and within a few years the dualistic theory was abandoned by all but its author, to be revived nearly half a century later, in a special form in application to ionic dissociation of salts in solutions, by another Swede, Arrhenius.

To explain the formation of hydrogen or alkali or deposition of metals at one electrode and of acid or oxygenous substances at the other electrode in electrolysis, Grotthus in 1806 suggested that the particles in solution acted as small dipolar magnets and arranged themselves into chains extending from electrode to electrode, the terminal polar parts of opposite sign being split off under the attraction of the oppositely charged electrodes.<sup>1</sup> Subsequent work has proved that infinitesimal amounts of electricity suffice to make evident the decompositions associated with electrolysis, and modern theories involve that the electrolyte is dissociated into polar parts in the act of solution and in the absence of an electric current, and **Grotthus' Hypothesis**, that the current causes the dissociation, thus appears to have no foundation. The modern theories are essentially a return to Davy's explanation of 1806 that chemical attraction between the particles of a substance is destroyed by imparting electric charges, and conversely that the particles are charged before decomposition by electrolysis.

In 1833 and 1834, Faraday investigated the quantities of the products of electrolytic decomposition produced by equal quantities of electricity, and discovered the two **Laws of Electrolysis**, that the amount of decomposition of a

<sup>1</sup> *Ann. Chem. Phys.*, 1806, [1], 53, 64, and 1807, [1], 63, 20.

given electrolyte is proportional to the quantity of electricity which flows through it, and that the quantities of different substances liberated by the same quantity of electricity are in the ratio of their chemical equivalents<sup>1</sup> Faraday assumed that the products of electrolysis could not appear at the electrodes without motion of parts of the electrolyte molecules from end to end of the liquid, and proposed the term "ions" (Greek = "*travellers*"), "anions" (Greek = "*upgoers*"), and "cations" (Greek = "*downgoers*"), the anions being those atoms or groups of atoms transported to the "anode" (Greek = "*up-path*") or positive electrode, and the cations those transported to the "cathode" (Greek = "*down-path*") or negative electrode, *anions* thus carrying *negative* and *cations* *positive* charges. He further suggested that the equivalent weights of substances were simply those quantities that contained equal quantities of electricity, and that the quantities of electricity carried determined the equivalent number and the chemical combining force. Though Faraday failed to discern the different valencies of atoms and the "*atomic*" nature of electricity, his theory of chemical combination, as due quantitatively to electrical forces, is the basis of all modern theories of chemical combination and atomic structure.

In 1849, Weber put forward a theory of electricity anticipating, by over half a century, a great part of recent theories of the structure of matter and the nature of electricity.<sup>2</sup> Weber regarded an electric current, not as a continuous movement of electricity, but as a movement of electrostatic charges, and assumed the existence of positive and negative "*atoms of electricity*," and suggested that they must possess electromagnetic mass in virtue of their velocity. He further assumed that only the negative atoms of electricity were associated with material atoms, the positive

<sup>1</sup> *Phil Trans Roy Soc*, 1833, 123, 23, 1834, 124, 77, and *Experimental Researches in Electricity*, London, 1839, 1, 107, 195, 215, 230, and 821

<sup>2</sup> *Leipzig Trans*, 1849, 1, and 1857, 5, 260, *Pogg Ann*, 1856, 99, 10, and *Werke*, 4, p 278

atoms of electricity being devoid of weight and revolving round the massive negative atom. Interchanging the electrical signs, Weber's theory of the atom is practically identical with the Thomson-Rutherford-Bohr theory of the present day.

In 1850, Williamson<sup>1</sup> advanced a theory of the constitution of molecules and the mechanism of "*double-decompositions*" practically identical with modern views as to mass action and ionic dissociation in solutions. He regarded hydrochloric acid, for example, not as immutable molecules of HCl but as undergoing a continuous process of decomposition and recombination, "*each atom of hydrogen constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine.*" He further regarded the theory of *static* atoms as unsafe and unjustifiable, and stated that "*the dynamics of chemistry will commence by the rejection of this supposition, and will study the degree and kind of motion which atoms possess, and reduce to this one fact the various phenomena of change.*"<sup>2</sup> His statement "*that metallic zinc is contained in its sulphate is only strictly true by abstraction from most of the properties of the metal. The material atom, which under certain circumstances possesses the properties which we describe by the word 'zinc,' is no doubt contained in the sulphate, but with different properties,*" is prophetic in view of the modern theory that the sulphate group contains two electrons abstracted from the atom of metallic zinc, thus converting the latter into a doubly-charged atomic ion having few of the properties of the original atom except weight.

In order to explain the fact of the small electric forces necessary for electrolytic decompositions, Clausius, in 1857, suggested that some of the molecules of the electrolyte are split up into ions in the act of dissolving, the phenomena of ionisation thus being strictly independent of electrolysis. He was unable to assign any definite value to the extent of

<sup>1</sup> See Chap. III, p. 39

<sup>2</sup> *Alcemic Club Reprints*, No. 16, pp. 15, 17, 19, 23, and 48.

ionisation, but assumed that it was infinitesimal, and that the ions, removed by discharge at the electrodes during electrolysis, were progressively replaced by further ionisation of the electrolyte<sup>1</sup>

Clerk Maxwell, in explaining the process of electrolysis, suggested in 1873 that "*each molecule, therefore, on being liberated from the state of combination, parts with a charge whose magnitude is  $\frac{1}{N}$* " ( $N$  = number of molecules in the

electrochemical equivalent), "*and is positive for the cation and negative for the anion. This definite quantity of electricity we shall call the molecular charge. If it were known it would be the most natural unit of electricity*"<sup>2</sup> He regarded the constant molecular charge or "*molecule of electricity*" merely as a convenient hypothesis for the explanation of electrolysis, and rejected it entirely in developing his "*Electromagnetic Theory of Light.*"

In 1874, Johnstone Stoney proposed a system of fundamental units of nature, the natural unit of quantity of electricity being that associated with the electrochemical equivalent in electrolysis. He stated, "*For each chemical bond ruptured in electrolysis a certain quantity of electricity traverses the electrolyte, which is the same in all cases.*" For this constant quantity of electricity he proposed the name "*electrine,*"<sup>3</sup> or electromagnetic unit of quantity. This name, in 1891, he altered to "**electron**"<sup>4</sup> in a paper suggesting the physical characteristics of the orbits of the electrical particles giving rise to the light radiation causing the sharp lines in optical spectra.

Apparently unaware of the suggestions of Clerk Maxwell and Johnstone Stoney, Helmholtz, in his Faraday Lecture to the Chemical Society in 1881, put forward a similar explanation of Faraday's laws of electrolysis. He regarded

<sup>1</sup> Clausius, *Pogg Ann*, 1857, 101, 388, and 347.

<sup>2</sup> *Electricity and Magnetism*, 1st Ed 1873, 3rd Ed, 1892, p 379

<sup>3</sup> *Brit Assoc. Rep*, 1874, Sect. A, 22, reprinted, *Phil Mag*, 1881, [5], 11, 381

<sup>4</sup> *Scient. Proc. Roy. Dublin Soc.*, 1891, 583.

the chemical equivalent of each ion in an electrolyte as being united to an electric equivalent or atom of electricity, and suggested "*that each unit of affinity that an atom can be said to possess represents a charge that may be termed one atom of electricity,*" thus identifying valency with units of electrical charge<sup>1</sup>

The answer to Clausius' problem, as to the extent of ionisation of salts in solution, was suggested in 1884 by Arrhenius,<sup>2</sup> who regarded electrolytes as being largely ionised in the act of dissolving, and as becoming more and more completely ionised with increasing dilution of the solution.

In 1885, van't Hoff put forward a kinetic theory of osmotic pressure based on the analogy between the process of vaporisation and the process of solution.<sup>3</sup> He showed that the analogy between solutions and gases is complete on the assumption that the molecules of the solute exert the same (osmotic) pressure as they would as a gas occupying the same volume as the solvent. This kinetic theory of osmotic pressure has enabled determinations of molecular weights to be made in the case of non-vaporisable substances, by reference to deviations (from the normal constants of pure solvents) in vapour pressure, boiling and freezing points of solutions, and solubility of solutions for other substances, these deviations being simple functions of the osmotic pressure.

In the case of electrolytes, the osmotic pressures are found uniformly to be abnormally high, and Arrhenius, by the application of his theory of ionisation, was able to show that the abnormality was due to the splitting of the electrolyte into ions, each ion contributing to the osmotic pressure an amount equal to that due to a non-ionised molecule.<sup>4</sup>

<sup>1</sup> *J Chem Soc*, 1881, 39, 302

<sup>2</sup> *Researches on the Conductivity of Electrolytes*, Stockholm, 1884, *Brit Assoc Rep.*, 1886, 357

<sup>3</sup> *K Svenska Vet-Akad Handl*, 1885, 21, 38, *Arch Néel*, 1886, 20, 239, and *Zeit phys Chem*, 1887, 1, 481

<sup>4</sup> *Zeit phys. Chem*, 1887, 1, 631.

As determinations of the degree of ionisation can be made on the assumption that the number of ions is proportional to the electrical conductivity of the solution, the molecular weights of ionisable substances can be determined by means of the conjoint hypotheses of van't Hoff and Arrhenius. In the hands of Werner and others, this method has given an insight into the constitution of complex compounds otherwise experimentally unobtainable.

In 1890, Ciamician suggested that ionisation of electrolytes (salts, acids, and bases) in solution is due to attraction between the molecules of the solvent and the positive and negative parts of the molecules of the electrolyte, thus bringing about rupture of the chemical molecules into separate charged parts or ions, each entirely surrounded by molecules of the solvent.<sup>1</sup> This suggestion is supported to some extent by the fact that those solvents with great ionising capacity usually unite with anhydrous salts to form crystalline complex molecules, e.g.  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , washing soda with *water* of crystallisation,  $\text{CaCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ , calcium chloride with *alcohol* of crystallisation,  $\text{MgI}_2 \cdot 6\text{CH}_3\text{COCH}_3$ , magnesium iodide with *acetone* of crystallisation,  $\text{AlBr}_3 \cdot \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ , aluminium bromide with *ether* of crystallisation,  $\text{NiSO}_4 \cdot 3\text{C}_3\text{H}_7\text{O}_3$ , nickel sulphate with *glycerine* of crystallisation,  $\text{CuSO}_4 \cdot \text{H}_2\text{O} \cdot 4\text{NH}_3$ , copper sulphate with both *water* and *ammonia* of crystallisation, and  $\text{CrCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ , chromic chloride with *pyridine* of crystallisation. Van der Waals, in 1891, put forward a similar theory of ionisation, and regarded the heat of hydration of salts as the source of the energy necessary to rupture the chemical molecule into oppositely charged ions.<sup>2</sup>

In 1891, Werner put forward a new theory of chemical affinity and valency,<sup>3</sup> in which he regarded the force of valency as being distributed over the surface of the atom and utilised in binding other atoms sufficient in number to

<sup>1</sup> *Zeit. phys. Chem.*, 1890, 6, 408.

<sup>2</sup> *Ibid.*, 1891, 8, 215.

<sup>3</sup> See his *Co-ordination Theory*, Ch. VII, page 81.

form an enclosing shell to the central attracting or co-ordinating atom. Anhydrous salts on solution were thus regarded as combining with the solvent molecules by means of some of their atoms, so that each central metallic atom completed its "*co-ordination number*" of atoms in the shell, the shell being formed partly or wholly of atoms derived from the solvent. If all the acidic atoms (or groups) of the original salt remain attached in the co-ordination shell no ionisation occurs, but, if one or more of the acidic atoms (or groups) be not bound in the shell, ionisation occurs, the central atom with its co-ordinated shell of atoms forming a complex positive ion, the acidic atoms (or groups) forming negative ions. This co-ordination theory was applied not merely to the phenomena of ionisation and electrolysis but to the constitution and reactivities of complex salts in general, and constitutes probably the most outstanding and fruitful contribution to the general theory of chemistry in the history of the science, and an interpretation of the theory in terms of the electronic nature of valency enables far-reaching deductions to be made as to the external and internal structure of the atoms of practically the whole of the known elements.

## VALENCY AND STEREO-CHEMISTRY

THOUGH Plato, about 400 B.C., had assigned to the primordial atoms the three-dimensional structures of the five regular solids, the *tetrahedron*, *octahedron*, *cube*, *icosahedron* and *dodecahedron*, having *four*, *six*, *eight*, *twelve*, and *twenty* point configurations respectively, these shapes were not assigned to the atoms on the grounds of any physical necessity occasioned by any known property of matter. Wollaston's recognition of the simple multiple combining capacities of carbonic, oxalic, and sulphuric acids,<sup>1</sup> and his suggestion as to the three-dimensional geometry of the primary particles of matter, probably constitute the earliest use of stereo-conceptions in the explanation of experimental facts. Wollaston said, "*when our views are sufficiently extended, to enable us to reason with precision concerning the proportions of elementary atoms, we shall find the arithmetical relation alone will not be sufficient to explain their mutual action, and that we shall be obliged to acquire a geometrical conception of their relative arrangement in all the three dimensions of solid extension . . . a stable arrangement may again take place, if the four particles are situated at the angles of the four equilateral triangles composing a regular tetrahedron . . . it is perhaps too much to hope, that the geometrical arrangement of primary particles will ever be perfectly known.*" However, forty-six years after Wollaston's death in 1828, van't Hoff and Le Bel simultaneously put forward complete explanations of the properties of organic substances based on the *tetrahedral* nature of the carbon atom, and, seventy-two years after the same date, Pope and Smiles (see page 46) simultaneously demonstrated the *tetrahedral* nature of the sulphur atom, and the tetrahedral structure of the carbon and sulphur atoms in Wollaston's polybasic carbonic, oxalic, and sulphuric acids is to-day no less firmly established than the reality of atomism.

The growth of the idea that the properties of compound

<sup>1</sup> *Phil Trans Roy Soc*, 1808 98, 96

are largely dependent on the arrangements of atoms is coincident with the growth of the conception of valency. Gay-Lussac's suggestion of 1824, as to the different arrangements of the atoms in silver fulminate and silver cyanate, was amplified by Berzelius in 1832 into a theory of isomerism. Laurent's "nucleus theory" of 1835 foreshadowed the carbon atom with a definite shape and capacity for spatial combination. Dumas' theory of "mechanical types" and "substitutions" and Laurent's "nucleus" theory emphasised the persistence and stability of the combinations of carbon atoms with one another. Pasteur's discovery in 1848 of the hemihedrism of optically active crystals and his researches in subsequent years led to the theory of molecular asymmetry and the tetrahedral structure of a large number of atoms. Liebig's theory of polybasic acids in 1838, Williamson's "water type" of 1850, Frankland's theory in 1852 of the definite combining capacity of atoms, and Gerhardt's theory of simple types of 1853, paved the way for Cannizzaro's, Kekulé's, and Couper's theory of "atomicity" or valency, in 1858, and within a few years definite valencies had been assigned to all the known elements.

In 1852, Frankland (E) suggested that "*the formation of a five-atom group, from one containing three atoms, can be effected by the assimilation of two atoms (or two semi-molecules) either of the same or of opposite electro-chemical character,*"<sup>1</sup> and in 1866 he amplified this suggestion in the statement: "*This variation of atomicity always takes place by the disappearance of an even number of bonds . . . one or more pairs of bonds belonging to an atom of the same element can unite, and, having saturated each other, become, as it were, latent.*"<sup>2</sup> This suggestion was revived in 1902 by Spiegel,<sup>3</sup> by Arrhenius in 1906,<sup>4</sup> and again by Friend in 1908,<sup>5</sup> as a

<sup>1</sup> *Phil Trans Roy Soc*, 1852, 142, 417

<sup>2</sup> *Lecture Notes for Chemical Students*, 1866

<sup>3</sup> *Zeit anorg Chem*, 1902, 29, 365

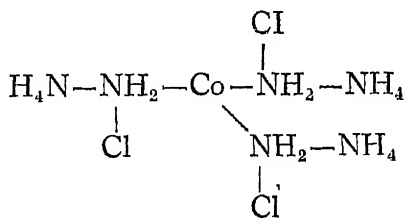
<sup>4</sup> *Theorien der Chemie*, Leipzig, 1906

<sup>5</sup> *J Chem Soc*, 1908, 93, 260

theory of "neutral affinities," "electrical double valencies," and "latent valency," and involved additional ordinary valences capable of being utilised in pairs of equal and opposite sign. In this form, however, the theory has proved sterile, and has led to much fruitless discussion, owing to the fact that many elements are known which have several *valencies differing not by two units but by one*, for example, the twenty-four elements of the three transition series of the periodic classification. Wiener, in his "co-ordination theory" adopted Frankland's suggestion and clearly elucidated its meaning. He showed that lower valency is converted into valency one or two units higher only when the element exhibits electropositive valency (metal-like), and that the increase in apparent valency by two units of equal and opposite sign is found only when the element exhibits electronegative valency (as a non-metal). He regarded the two apparent valences as dissimilar in function, one of the atoms added being held by "**residual affinity**" of the central electronegative atom and the other appearing as an electronegative ion. On this basis he elaborated a theory of the constitution of metal compounds with ammonia and water, deriving them from the simple ammonium type, the apparent additional valences of the combined ammonia groups being utilised not necessarily in pairs but even in parts of a single valence. Positively trivalent nitrogen in nitrous anhydride,  $N_2O_3$ , by the addition of two equivalents of oxygen per atom of nitrogen, yields nitric anhydride,  $N_2O_5$ , containing positively quinquevalent nitrogen. Negatively trivalent nitrogen in ammonia,  $NH_3$ , on the other hand, cannot be induced to yield a negatively quinquevalent derivative. It combines with hydrochloric acid,  $HCl$ , to yield ammonium chloride,  $NH_4Cl$ , in which the negative chloride atom ionises from the positive ammonium group,  $NH_4$ , on solution in water. Wiener postulated that the hydrogen atom from  $HCl$  is added to  $NH_3$  *without alteration in nitrogen valency*, merely by the general attraction between the positive hydrogen

atom and the negative nitrogen atom, but that, once combination is effected, all four hydrogen atoms in the  $\text{NH}_4$  group are identically bound to the nitrogen atom. This conception, difficult as it then seemed, has in recent years, by chemical and physical methods, been fully confirmed, and, in the electronic interpretation of valency, is seen to be remarkably simple. Werner further postulated that the metal amines, for example, hexamminocobaltic chloride,  $\text{CoCl}_2 \cdot 6\text{NH}_3$ , are also ammonium compounds, one-sixth of a cobalt atom taking the place of a hydrogen atom in ammonium,  $\text{NH}_4$ , so that the complex compound could be regarded as  $6(\text{NH}_3\text{Co}^{\frac{1}{6}})\cdot\text{Cl}_2$ , or  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ . In this case six ammonia molecules add three equivalents of cobalt and three chlorine atoms, or each ammonia molecule adds only one-half of a positive valency plus one-half of a negative valency. This interpretation rendered impossible the existence of *latent valencies in pairs of equal and opposite sign*, and confirmed Werner's view that valency, once called into operation, is a force distributed over the surface of an atom and is independent of the atoms to which it owes its origin. This theory necessitated the distribution of the valency forces in space, and led to the **octahedral** structure of many atoms, a structure which has been demonstrated beyond any possibility of doubt by Werner and others from considerations based on geometrical and optical isomerism.

In 1854, Hofmann suggested that the ammonia compounds with metallic salts were derived from the pentad nitrogen type, and luteo or hexamminio-cobalt chloride having the following formula,  $\text{Co}(\text{NH}_2\text{Cl}\cdot\text{NH}_4)_3$ , or



This suggestion was elaborated into a complete scheme of chain-formulæ by Blomstrand in 1869,<sup>1</sup> and was adopted generally, until Werner's demonstrations of the spatial structure of these complexes brought about the downfall of Blomstrand's theory. The authority of Blomstrand and Jørgensen, to the latter of whom chemistry early owes the preparation of the bulk of the metalammunes, was sufficient to maintain the plane chain-formulæ for over forty years and retarded the application of spatial ideas of molecular structure in inorganic chemistry for at least a generation. Even as late as 1910 authoritative adherents were to be found in this country for Blomstrand's formulations, with the result that Werner's theory of molecular structure was held in suspicion, and its application to atomic structure delayed till after Werner's death in 1919.

In 1857, Gibbs and Genth, in their epoch-making researches on the ammonia-cobalt bases,<sup>2</sup> referred to the cobalt atom as "hexatomic," despite their recognition that the combining capacity of cobalt was three. They apparently distinguished the trivalency of cobalt in its combination with oxygen or acid radicals from the six groups forming the "conjunct" with the cobalt atom, and regarded the molecules as containing only one atom of cobalt. Their views were a remarkable foreshadowing of Werner's co-ordination theory of thirty-four years later and had Gibbs not subsequently embraced Blomstrand's theory of chain-formulæ and two cobalt atoms per molecule, it is probable that a co-ordination theory would have been evolved long before 1891.

The development of ideas as to the spatial arrangement of carbon atoms in organic compounds was very rapid after Kekulé's exposition of his theory of "atomicity" (valency) in 1858. Butleroff, in 1860, viewed the "structure" or mode of linking of carbon atoms as of prime importance and in 1863, Wislicenus, referring to the existence of iso

<sup>1</sup> *Chemie der Jetztzeit*, Heidelberg, 1869.

<sup>2</sup> *Smithsonian Contributions to Knowledge*, Washington, 1857, IX.

meric forms of lactic acid,<sup>1</sup> stated that the existence of isomers was due to change in the order of distribution of atoms in space, whereas formulæ represent only a picture of a molecule in one plane. In 1866, Kekulé suggested the cyclic formula for benzene, which, with very slight modification, represents accurately the views of chemists at the present day.<sup>2</sup> In the following year Kekulé suggested that the four units of affinity of the carbon atom projected from the surface in the direction of the four faces of a **tetrahedron**.<sup>3</sup> In 1869, Paterno suggested that, if the four valences of carbon were directed towards the corners of a tetrahedron (Diagram I, p. 64), the formula  $C_2H_4Cl_2$  should represent three isomeric substances. In 1873, Wislicenus, to whom chemistry is largely indebted for the experimental elucidation of the arrangement of carbon atoms in many organic compounds, suggested the term "**geometrical isomerism**" to cover the cases of compounds identical in composition and differing only in the arrangement of the atoms in space.<sup>4</sup> This term was altered in 1888 by Victor Meyer to "**stereo-isomerism**" to cover all cases of spatial isomers, "geometrical isomerism" being retained for the special cases associated with double bonds between atoms, and "**optical isomerism**" for those cases in which the only difference in the properties of the isomers is their opposite rotatory effect on polarised light.

Within a few months of one another in 1874, van't Hoff in Holland and Le Bel in France published almost identical theories of the tetrahedral structure of carbon atoms. Van't Hoff apparently regarded the carbon atom as being a tetrahedral shaped piece of matter,<sup>5</sup> whereas Le Bel regarded the carbon atom as a centre of attraction round which four other atoms could be arranged with tetrahedral

<sup>1</sup> *Ann*, 1863, 128, 1.

<sup>2</sup> *Ibid*, 1866, 137, 160, and 229

<sup>3</sup> *Zeit Chem*, 1867, new series 3, 217

<sup>4</sup> *Ann*, 1873, 167, 345

<sup>5</sup> *Voorstel tot uitbreiding der structuurformules in de ruimte*, Sept, 1874

symmetry.<sup>1</sup> Both theories gave a complete explanation of isomerism in organic compounds, van't Hoff's theory being more particularly directed to the explanation of geometrical isomerism and Le Bel's to optical isomerism, the former being influenced largely by the work of Kekulé and Wislicenus and the latter by that of Pasteur.

In 1869, Blomstrand<sup>2</sup> pointed out that the most strongly electropositive and electronegative elements possessed the smallest saturation capacity (valency), the highly positive alkali metals, for example, combining with great energy with the highly negative halogen elements to form compounds containing one atom of each per molecule. No explanation of this circumstance appears to have yet been given, and it constituted the chief reason for the reluctance of chemists to accept the electrical theories of Helmholtz and others that chemical forces are entirely electrical in origin, for the variability in intensity of chemical force with valency appeared incompatible with invariable electrical charge per valence. The variations in intensity of chemical forces are now known to be closely connected with the capacity of elements to form ionisable compounds, or in terms of Werner's co-ordination theory, with the capacity of atoms for stable co-ordination with other atoms thus disclosing the features of their superficial structure. The alkali metals and the halogens almost alone of the elements give rise to atomic ions in solutions, form easily hydrolysable complex compounds, and give no indication, chemically, of possessing any structure other than that of uniform spherical surface. There is, consequently, practically no stereo-chemistry of the alkali metals or the negative ions of the halogens.

In 1881, van't Hoff suggested that valency is a function of the shape of an atom, and that variable valency is associated with variation in the atomic shape.<sup>3</sup> He stated

<sup>1</sup> Le Bel, *Bull. Soc. Chim.*, 1874 (Nov.), 22, 337

<sup>2</sup> *Loc. cit.*, p. 60

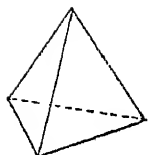
<sup>3</sup> *Ansichten über die organische Chemie*, 1881, XI, 3

that "an atom of such a shape (triangular) would therefore comport itself generally as trivalent and occasionally as sexavalent, and, it should be noted in this connexion, that, just as the number and kind of the valences may be deduced from the shape of the atom, so conversely the shape of the atom might be deduced from an accurate knowledge of its valency." Ten years later Le Bel<sup>1</sup> showed that methyl-ethyl-propyl-isobutyl-ammonium chloride could be obtained in optically active forms, thus demonstrating that the central nitrogen atom can give rise to optical isomers. Werner later showed that the dissociation of this and similar ammonium compounds into a *complex ion* and a *halogen ion* necessitated that the nitrogen atom, like carbon, possesses *tetrahedral symmetry*, and this conclusion has since been amply confirmed.

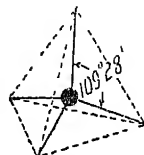
If the four valences of the carbon atom are directed from the centre to the four corners of a regular tetrahedron (see Diagram I, p. 64), it can be proved geometrically that the angle between any two of the valences must be  $109^{\circ} 28'$ . If, further, two carbon atoms in combining by means of a single bond have the direction of the two separate valences united into a straight line between the centres of the atoms it is impossible for a chain of carbon atoms to complete a ring, for the angles of an equilateral triangle, square, pentagon, and hexagon are respectively  $60^{\circ}$ ,  $90^{\circ}$ ,  $108^{\circ}$ , and  $120^{\circ}$ . Compounds are well known, however, in chemistry containing closed rings of three, four, five, and six carbon atoms. The smallest deviation from the tetrahedral angle of  $109^{\circ} 28'$  is consequently that of the five-membered ring of  $108^{\circ}$ . In 1885, Baeyer put forward a theory, known as "**Baeyer's Strain Theory**," that the valences of the carbon atoms are strained out of the position of tetrahedral equilibrium by implication of the atoms in cyclic structures, the strain being *least* for the *five-membered cyclo-pentane ring*, and *greatest* for the *three-membered cyclo-propane ring*, other rings showing an intermediate degree of strain in propor-

<sup>1</sup> *Compt. rend.*, 1891, 112, 725

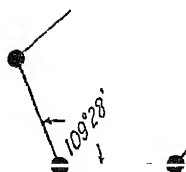
DIAGRAM I



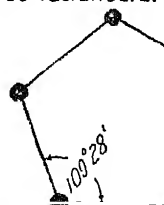
Tetrahedron



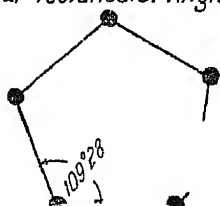
Tetrahedral Valences



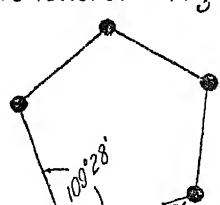
Three Tetrahedral Angles



Four Tetrahedral Angles

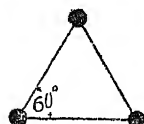


Five Tetrahedral Angles

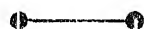


Six Tetrahedral Angles

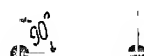
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Cyclopropane Ring

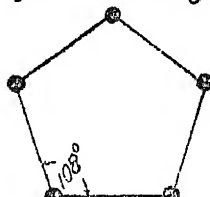


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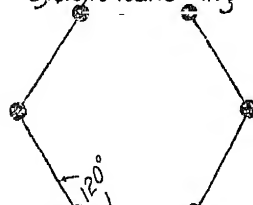
Cyclobutane Ring

→



Cyclopentane Ring

→



Cyclohexane or Benzene Ring

tion to the deviation of the polygonal angle from the tetrahedral angle. This theory accords fairly well with the known ease or difficulty of formation and of disruption of cyclic structures.<sup>1</sup> This theory has undergone considerable modification in the last five years as a result of the work of Thorpe (J. F.) and Ingold and their collaborators,<sup>2</sup> who have proved that the strain on two carbon valences implicated in an open-chain or a cyclic structure can be relieved by the utilisation of the other two valences in binding other atoms (or groups of atoms) of appropriate volume, the angle between these two valences being  $115.3^\circ$  for hydrogen atoms,  $109.5^\circ$  for methyl groups, and still smaller angles for larger groups or for a ring of carbon atoms. These investigations promise to throw considerable light on deviations of the structure of the surface of carbon atoms from tetrahedral symmetry, and, inferentially, on the nature and stability of the electronic orbits in atoms.

<sup>1</sup> *Polyacetylene Compounds*, 1885, and *Ber.*, 1885, 18, 2277

<sup>2</sup> *J. Chem. Soc.*, 1919, 115, 320, 1920, 117, 591, etc

## CHAPTER VI

### CLASSIFICATION OF THE ELEMENTS

THE earliest attempts to classify elements probably date back to the discovery of metals and their recognition as single substances. The metals were originally classified as *noble* and *base*, the former including gold and silver, and the latter copper, iron, lead, tin, and mercury. Until, however, the criteria for the distinction of elements from compounds were established towards the end of the eighteenth century, no further advances in the classification of elements were possible.

In 1789, Lavoisier<sup>1</sup> arranged the elements into four classes: (1) light, heat, and the three gases, oxygen, nitrogen, and hydrogen; (2) non-metallic solids, such as sulphur, phosphorus, and carbon; (3) metals, such as copper, iron, lead, gold, silver, and mercury; and (4) "*earths*," such as lime, baryta, magnesia, alumina, and silica. The "*earths*," and light and heat are, however, no longer regarded as elements, and the two last are not even material substances.

Berzelius based his "*Dualistic Theory*"<sup>2</sup> on Lavoisier's classification, with such amendments as the intervening years had rendered necessary, the elements being divided into electropositive and electronegative groups, which coincided largely with the groups of metallic and non-metallic elements.

In 1815, Prout<sup>3</sup> basing his ideas on Dalton's atomic weights as amended by the more accurate work of Berzelius, suggested that the atomic weights of all the elements were exact multiples of the atomic weight of hydrogen. Though **Prout's Hypothesis** was strongly supported, particularly by Thomson (T.), it was regarded by Berzelius in 1827 as having no foundation. Attempts were made at various times (Dumas and Stas in 1841, and Maignac in 1842 and 1860) in the nineteenth century to revive the hypothesis,

<sup>1</sup> *Traité élémentaire de Chimie*, Paris, 1789

<sup>2</sup> See Chap. IV, p. 48

<sup>3</sup> *Thomson's Ann. Phil.*, 1815, 6, 321, and 1816, 7, 111.

which was finally abandoned by chemists after Stas' extremely refined determinations of atomic weights in 1860 had demonstrated that many atomic weights were not even approximately integers. A modification of this hypothesis was put forward in 1896 by Lothar Meyer, who suggested that all atoms are composed of hydrogen atoms combined with varying amounts of the "*luminiferous ether*," which he thought might not be entirely devoid of weight. Lothar Meyer's suggestion has not been accepted by chemists generally, but recent speculations on the structure of matter and the nature of energy have lent considerable support to it, in the sense that all mass may be a manifestation of the inertia of specialised portions of the ether, decrease in inertia resulting on very close juxtaposition of such specialised portions of the ether. The modern theory of isotopes and inferences from radio-activity and the artificial disintegration of atoms have, however, brought about a more direct return to Prout's hypothesis, and non-integral atomic weights are now regarded as average atomic weights due to mixtures of atoms of integral atomic weight.

In 1817, Dobereiner observed that groups of three closely related elements have either nearly the same atomic weight or have atomic weights showing an approximately constant difference, for example, iron, cobalt, and nickel, with atomic weight about 58, and calcium, strontium, and barium, with atomic weights differing by about 48, chlorine, bromine, and iodine with difference about 46, lithium, sodium, and potassium with difference about 16, and sulphur, selenium, and tellurium with difference about 48.<sup>1</sup> Dumas extended Dobereiner's Triads by including fluorine with chlorine, bromine, and iodine, oxygen with sulphur, selenium, and tellurium; and nitrogen with phosphorus, arsenic, and antimony.<sup>2</sup>

<sup>1</sup> *Gilbert's Ann*, 1817, 56, 332, and 57, 436, and *Pogg Ann*, 1829, 15, 301

<sup>2</sup> *Traité de Chimie appliqué aux Arts*, Paris, 1828, *Bull Assoc Rep*, 1851, *Compt. rend*, 1857, 45, 709, 1858, 46, 951, and 47, 1026, *Ann. Chim Phys* 1859, [3], 55, 129

Gmelin,<sup>1</sup> in 1843, further extended Dobereiner's suggestions and devised a system of classification of the elements based on family relationships between elements, similarities in chemical properties appearing after certain increases in atomic weight. In 1845, Faraday showed that elements could be classified in two series, (1) paramagnetic elements attracted by a magnet, and (2) diamagnetic elements repelled by a magnet, and, in 1852, he further showed that this classification included in the same series those elements exhibiting close chemical similarity.<sup>2</sup>

Pettenkofer re-examined the numerical relationships between Dobereiner's triads and other chemically related elements, and in 1850 suggested that chemically similar elements formed series in which their atomic weights could be derived as a modified arithmetical progression involving the lowest atomic weight and multiples of an integer; and modifications of **Pettenkofer's Series** were proposed from time to time until the general law underlying the classification of the elements was discovered.<sup>3</sup> In 1854, Cooke<sup>4</sup> showed that Dobereiner's triads were merely parts of series, and that each series followed a simple algebraic law in the increase of atomic weight.

In 1857, Odling arranged the elements into thirteen classes according to similarities in chemical and physical properties, each class being arranged in the order of atomic weights.<sup>5</sup> Though this classification included the various groups of elements chemically closely related, it failed to show any relationship between atomic weights and chemical properties. It is, however, practically identical with the classification now in use for grouping the elements for qualitative analysis, and included silver, lead, and mercury, which give insoluble chlorides; arsenic, antimony, and

<sup>1</sup> *Handbuch der Chemie*, Heidelberg, 1843.

<sup>2</sup> *A Course of Six Lectures on the Non-metallic Elements*, London, 1852.

<sup>3</sup> Pettenkofer, *The Regular Intervals in the Equivalent Weights of Elements*, 1850, and *Ann.*, 1858, 105, 187.

<sup>4</sup> *Amer. J. Sci.*, 1854, [2], 17, 387.

<sup>5</sup> *Phil. Mag.*, 1857, [3], 13, 280, and 420.

bismuth giving sulphides insoluble in dilute acids ; chromium, manganese, and iron giving hydroxides insoluble in ammonia ; calcium, strontium, and barium giving insoluble carbonates ; and lithium, sodium, and potassium having soluble salts. It has been suggested that Odling's system, revised in the light of existing knowledge, would furnish the most convenient system for the classification of chemical knowledge of the elements, but its inherent defect is its failure to indicate periodicity of chemical properties with atomic weights, and, had it been adopted, it is extremely doubtful if it could in any way have assisted in elucidating the structure of atoms, which has been deduced almost solely from the periodic classification.

In 1862, de Chancourtois proposed a classification of the elements based on the new values of atomic weights consequent on Cannizzaro's system of 1858. De Chancourtois plotted the values of the atomic weights on a helical curve described on a cylinder, such that corresponding points on the curve differed by sixteen, the atomic weight of oxygen. This curve, called by him the "*vis tellurique*" or "*telluric screw*," brought into the same column many elements chemically closely related, and, in consequence, he suggested that "*the properties of the elements are the properties of numbers.*"<sup>1</sup>

In 1863, Newlands proposed a system of classification of the elements in the order of atomic weights, the elements being divided into seven groups having chemical properties analogous to the first seven elements, hydrogen, lithium, glucinum (sometimes called beryllium), boron, carbon, nitrogen, and oxygen.<sup>2</sup> Newlands termed this septenary relationship the **Law of Octaves**, by analogy with the seven intervals in the octave of the musical scale. He further assigned to the elements in the order of their

<sup>1</sup> *Compt rend*, 1862, 54, 757, 840, 967, 55, 600, 1863, 58, 253, 467, 1217, *Vis tellurique, classement naturel des corps simples ou radicaux obtenu au moyen d'un système de classification hélicoïdal et numérique*, Paris, 1863

<sup>2</sup> *Chem News*, 1863, 7, 70, 1864, 10, 59, 94, 95, 240, 1865, 12, 83, 94, 1866, 13, 113, 130, *On the Discovery of the Periodic Law*, London, 1884

atomic weights, a series of numbers beginning with hydrogen 1. This system of assigning ordinal numbers to the elements was revived fifty years later by Van den Broek, who identified the ordinal number with the charge on the atomic nucleus and with the number of electrons in the neutral atom, and the **Atomic Number** of an element is regarded to-day as an atomic constant no less important than atomic weight or valency. Newlands' classification and law of octaves were unfortunately regarded with extreme derision, and he abandoned further pursuit of the remarkable relationships he had discovered. The attitude of chemists in this country to Newlands' proposals is a conspicuous example of the truth of the proverb about *unhonoured native prophets*, for an almost identical proposal six years later by the Russian chemist, Mendeléeff, immediately gained general acceptance.

In 1864, Odling proposed a classification of the elements very similar to that of Newlands, and suggested that "*Doubtless some of the arithmetical relations exemplified in the foregoing table are merely accidental, but, taken altogether, they are too numerous and decided not to depend on some hitherto unrecognised law.*"<sup>1</sup> Even Odling's authority, however, failed to make the proposals acceptable, and the law died still-born.

In March, 1869, Mendeléeff communicated to the Russian Chemical Society a paper, *The Correlation of the Properties and Atomic Weights of the Elements*,<sup>2</sup> in which he showed that "*the elements arranged according to the magnitude of atomic weight show a periodic change of properties,*" and put forward a table of the elements arranged in groups practically identical with those of Newlands and Odling. The groups in their three tables were arranged horizontally, an arrangement altered by Mendeléeff in 1871 to the now familiar form of vertical groups and horizontal rows, or series.

<sup>1</sup> *Watts's Dictionary*, 1864, 3, 975, *Quart J Sci*, 1864, 1, 643

<sup>2</sup> *J Russ Chem Soc*, 1869, 1, 60, 1870, 2, 14, 1871, 4, 25, and 348

TABLE I.—MENDELÉEFF'S TABLE OF 1871

Row	Group I R <sub>2</sub> O	Group II RO	Group III R <sub>2</sub> O <sub>3</sub>	Group IV RH <sub>4</sub> RO <sub>2</sub>	Group V RH <sub>3</sub> R <sub>2</sub> O <sub>5</sub>	Group VI RH <sub>2</sub> RO <sub>2</sub>	Group VII RH R <sub>2</sub> O <sub>7</sub>	Group VIII RO <sub>4</sub>
1	H=1	—	—	—	—	—	—	—
2	Li=7	Be=9 4	B=11	C=12	N=14	O=16	F=19	—
3	Na=23	Mg=24	Al=27 3	Si=28	P=31	S=32	Cl=35 5	—
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Ni=59
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	Co=59 Cu=63
6	Rb=85	Sr=87	Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104 Pd=106
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	Rh=104 Ag=108
8	Cs=133	Ba=137	Di=138	Ce=140	—	—	—	—
9	—	—	—	—	—	—	—	—
10	—	—	Er=178	La=180	Ta=182	W=184	—	Os=195 Pt=198
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	Ir=187 Au=199
12	—	—	—	Th=231	—	U=240	—	—

In this table Mendeléeff differentiated the members of some of the groups into two classes according to whether they belonged to series with *odd* or with *even* number, group II, for example, containing two subgroups, the first with beryllium, calcium, strontium, and barium in the series of even number, and the other with magnesium, zinc, cadmium, and mercury in the series of odd number. This differentiation of the members of odd and even series is possibly more remarkable than the differentiation into groups and series, and serves to emphasise the outstanding nature of Mendeléeff's genius. He thus regarded some sets of two series, one even and one odd, for example, 4 and 5, 6 and 7, 8 and 9, and 10 and 11, as together forming single *periods* of seventeen elements, series 2 and 3 being separate groups of seven each. This differentiation has in very recent years proved to be of fundamental importance in the determination of the electronic structure of atoms, being the sole known criterion for the separation of the atomic elections into groups containing the maximum possible number of electrons. Even more remarkable than the differentiation of the **Periodic groups** into even and odd series, was Mendeléeff's suggestion as to the so-called transition elements. It is commonly but wrongly stated that the transition elements are those of group VIII, and that they form a transition group from the even to the next odd series. This was not Mendeléeff's view, but that of lesser minds with weaker vision. He actually made use of the following words, "*the following transition period: Cr = 52, Mn = 55, Fe = 56, Co = 59, Ni = 59; Cu = 63; Zn = 65*", and the members of group VIII, the triads, Fe Co Ni, Ru Rh Pd, and Os Ir Pt, he termed "*intermediate series of elements*." His "**transition periods**" are almost identical with those in Bohr's theory of atomic structure, in which the transition periods represent the extension of an incomplete but stable group of electrons into a group with the maximum possible number of electrons. Bohr differed from Mendeléeff merely in the precise

extent of the transition period, scandium, titanium, and vanadium, for example, being also included, and zinc excluded from the first transition period. It is, however, probable that Bohm is correct in the extent of the transition series. Evidence for this will be given in Chapters XIII and XIV.

In December, 1869, ten months after the appearance of Mendeléeff's first paper, Lothar Meyer<sup>1</sup> put forward views, probably independently, almost identical with Mendeléeff's. Lothar Meyer appears to have come to his conclusions largely from the consideration of the physical properties of the elements, whereas Mendeléeff was guided almost entirely by considerations based on the chemical properties of the elements. To this extent they may be regarded as having discovered independent **laws of the periodicity of the properties of the elements** with atomic weight, the first the periodicity of chemical properties and the other the periodicity of physical properties. Lothar Meyer's views, however, disclosed a much less clear picture of the detailed nature of the periodicity, and completely disregarded the fundamental differentiation into even and odd series and the importance of the transition periods. The essential point common to both theories was the importance of valency in the determination of periodic properties, and the recognition of the increase in positive valency from 1 to 8 in passing from group I to group VIII, and the increase in negative valency from 1 to 4 in passing in the reverse direction from group VII to group IV.

Following the formulation of the **Periodic Law and Classification** by Mendeléeff, numerous variations in the form of the periodic table were proposed. The following table due to Bayley<sup>2</sup> is of interest as indicating clearly the distinction between Mendeléeff's even and odd series and his short and long periods.

<sup>1</sup> *Ann Supp*, 1870, 7, 354

<sup>2</sup> *Phil Mag*, 1882, [5], 13, 26

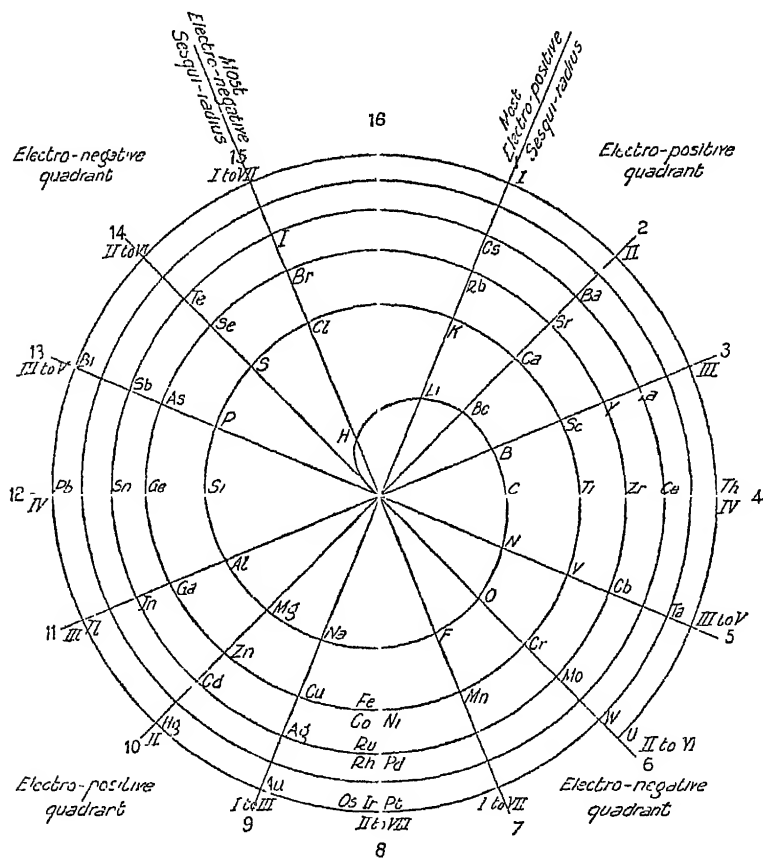
TABLE 2

[illegible]

## Bayley's Periodic Table

The periodic relationships were set out by various writers on a helix after the manner of de Chancourtois and on other forms of geometrical curves, the underlying idea being to illustrate some assumed mathematical function of the increases in atomic weight. The majority of these

DIAGRAM II



formulations of the periodic law offered no advantages over the tabular form, with the exception of the logarithmic spiral curve of Johnstone Stoney,<sup>1</sup> shown in Diagram II. This curve has the advantages not only of representing the

magnitude of the atomic weights and the periodicity of properties, especially valency, but left sesqui-radius 1 unoccupied, this being filled in 1902 by the inclusion of the five recently discovered "inert gases," helium, neon, argon, krypton, and xenon, having zero valency and no chemical properties. It is remarkable that Johnstone Stoney in 1888 did not discern something of the meaning of the unoccupied sesqui-radius, which being a continuation of radius 8 might have been predicted for the accommodation of from five to seven elements of valency zero or eight.

In 1895, Thomsen,<sup>1</sup> as the result of an argument on the change in nature of valency from the electronegative univalent halogen elements to the electropositive univalent alkali elements, put forward the view of "*the probability of the existence of a group of inactive elements*." In the same year, argon, the commonest of the inert gases, was discovered by Rayleigh and Ramsay,<sup>2</sup> and within six years the remaining four (or five including radon, the radium emanation), inert gases had been discovered by Ramsay, who created for them a new group O in the periodic table. Recent theories of the structure of atoms, however, indicate that these five or six inert gases would be more logically included in group VIII, despite their lack of valency, as being elements marking definite stages in the completion of electronic groupings in atoms. In either case, Mendeléeff's groups are increased from 7 to 8 for the short periods and from 17 to 18 for the long periods.

During recent years many variations of Mendeléeff's periodic table have been put forward. Most of these tables, being based on non-chemical theories of atomic structure, in their arrangement of the elements, cease to exhibit the fundamentally important point of classification of the elements according to similarity in chemical and physical properties. The primary object of any system of classification is to condense a multitude of facts into groups

<sup>1</sup> *Zeit anorg Chem*, 1895, 9, 283

<sup>2</sup> *Proc Roy Soc*, 1895, 57, 265

containing closely related facts, in order to facilitate apprehension, memory, and the utilisation of knowledge. This object cannot be attained in chemistry by any system of classification which fails to include in a group the maximum number of elements exhibiting marked similarity in qualitative and quantitative chemical and physical relationships. Mendeléeff's classification involved the division of each *long period* into two chemically similar series, distinguished as *even* and *odd* series, this division thus bringing closely related elements with the same valency into the same periodic group. The variations of Mendeléeff's table usually involve the extension of the *long periods*, so that the table is duplicated, as in Bayley's form, utilised by Bohr and others to exhibit resemblances in the structure of atoms. This divorcement of the *even* and *odd* series fails to make apparent the extraordinary resemblance between phosphates and vanadates, sulphates and chromates, perchlorates and permanganates, and between the "*noble metals*" of the eighth group and the "*noble gases*," and fails to make any contribution to the theory of atomic structure that is not more clearly apparent in Mendeléeff's table. Table 3 on page 79 very closely follows Mendeléeff's arrangement of 1871, and enables not only the whole of the chemical relationships between elements to be clearly discerned, but also serves as a basis for the interpretation of atomic structure even more complete than any inferred from the separation of the *even* and *odd* series of the *long periods* consequent on mathematical functions based on atomic numbers or atomic weights.

The arrangement of the elements shown in Table 3 is based solely on the classification of the elements according to similarities in chemical and physical properties, and is independent of any theory of the structure of atoms. Most of the chemical classifications of elements, based on atomic structure, give undue prominence to the "*inert or noble gases*," which are, in fact, relatively of little importance in nature and in chemical theory and practice. With the

exceptions of helium and neon, none of these elements is of direct importance in modern theories of the structure of atoms, for only these two are regarded as marking completed groups in electronic structures. The "*noble metals*," gold, platinum, iridium, osmium, silver, palladium, rhodium, and ruthenium, with which may be included copper, nickel, cobalt, and iron, are, on the other hand, not only important in nature and in chemistry, but fundamentally important in theories of atomic structure, and mark decisively the points at which groups of electrons are completed in the structure of atoms. The inclusion of both the "*noble gases*" and the "*noble metals*" in the same periodic group 8, is therefore necessitated in the classification of the elements according to chemical properties and according to atomic structure. Mendeléeff's division of the "*long periods*" into *even* and *odd* series of over fifty years ago is to-day abundantly justified, and, though he later failed to appreciate the close relation between the "*noble metals*" and the "*noble gases*," the soundness of his chemical instinct and the brilliance of his genius are almost unique in the history of the science.

TABLE 3.—PERIODIC CLASSIFICATION

Group	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3 to 5	2 to 6	1 to 7	zero to 8
1st short period	(H)						H	He
2nd short period	Li	Be	B	C	N	O	F	Ne
3rd short period	Na	Mg	Al	Si	P	S	Cl	A
4th short period								
1st long period	K	Ca	Sc	Ti	V	Cr	Mn	FeCoNiCu
2nd long period	{Cu}	Zn	Ga	Ge	As	Se	Br	Kr
3rd long period	Rb	Sr	Y	Zr	Cb	Mo	—	RuRhPdAg
4th long period	(Ag)	Cd	In	Sn	Sb	Te	I	Xe
5th long period								
6th long period	Cs	Ba	<sup>1</sup> Lā	Ct	Ta	W	—	OsIrPtAu
7th long period	{Au}	Hg	T	Pb	Bi	—	—	—
Last period	—	Ra	—	Th	—	U	—	—

<sup>1</sup> Lā includes the fourteen "rare earth" elements, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, all of which are characteristically trivalent. The last thirteen of these, many of which possess variable valency, may be regarded as a "transition series" between lanthanum and cerium, in the same way that the tetrads of elements in group 8 may be regarded as transition series between the septavalent elements of group 7 and the bivalent elements of group 2.

## CHAPTER VII

### WERNER'S CO-ORDINATION THEORY

FRANKLAND's recognition in 1852 of the definite numerical combining capacity of metallic and organic radicals laid the foundation for Gerhardt's theory of "hydrogen atomicity" in 1853, elaborated in 1858 by Cannizzaro, Kekulé, and Couper into the modern theory of integral valency. Owing to the fact that Kekulé's work lay almost entirely in the field of carbon chemistry, his views on valency were coloured very largely by the evidence of the invariable quadrivalency of carbon, and he regarded the valency of all elements as a constant atomic property. Confronted with the existence of such compounds as the trichloride and pentachloride of phosphorus, he revived Berzelius' conception of *second order* combinations, phosphorus pentachloride,  $\text{PCl}_5$ , being regarded as an addition compound of a molecule of the trichloride,  $\text{PCl}_3$ , and a molecule of chlorine,  $\text{Cl}_2$ . This conception of "*molecular compounds*" was used to explain the existence of all chemical compounds to which a rational formula could not be assigned on considerations of fixed integral valency. Kekulé's views continued to dominate the theory of complex compounds, hydrates, ammines, polyhalides, double salts, complex acids, and molecular addition compounds generally, for over thirty years.

The preparation in 1876 of the very stable gaseous phosphorus pentafluoride,  $\text{PF}_5$ , by Thomsen (T.E.), definitely refuted the idea that valency is an immutable property of atoms, and thereafter, though valency continued to be regarded as a numerically integral property of atoms, definite valency formulations were assigned to many compounds previously regarded as molecular addition compounds.

One of the chief criteria for the distinction of true valency compounds from molecular addition compounds was the alleged instability or ease of dissociation of the latter as compared with the former. Many facts, however, accumulated to show that this criterion was invalid.

Hexammino-cobaltic chloride,  $\text{CoCl}_3 \cdot 6\text{NH}_3$ , for example, is very stable, whereas cobaltic chloride  $\text{CoCl}_3$  is non-existent; sodium platinichloride,  $\text{PtCl}_4 \cdot 2\text{NaCl}$ , evolves no hydrochloric acid on treatment with concentrated sulphuric acid, though common salt,  $\text{NaCl}$ , a typical valency compound, is instantly decomposed, potassium ferrocyanide,  $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$ , yields no prussic acid,  $\text{HCN}$ , on treatment with cold acids, whereas potassium cyanide,  $\text{KCN}$ , evolves prussic acid even with so feeble an acid as carbonic, aluminium fluoride,  $\text{AlF}_3$ , is decomposed instantly with violence by water, whereas sodium aluminifluoride,  $\text{AlF}_3 \cdot 3\text{NaF}$ , is the inert mineral cryolite, boron trimethide,  $\text{B}(\text{CH}_3)_3$ , is a spontaneously inflammable gas, whereas its ammine,  $\text{B}(\text{CH}_3)_3 \cdot \text{NH}_3$ , is sufficiently stable to be volatilised unchanged. Such instances of the stabilisation of true valency compounds, by conversion into molecular addition compounds, can be multiplied a thousand-fold, and there is no reason to suppose that the nature or intensity of the forces causing combination in molecular addition compounds is differentiable from those in true valency compounds.

Considerations such as the foregoing led Werner in 1891<sup>1</sup> to propose a theory of chemical affinity and valency in which all chemical combinations were assigned to the same ultimate cause, the creation of atomic attractive forces by the bringing into operation of integral valency. On the setting up of integral valency, forces arise on the atoms concerned in the valency exchange, each atom becoming the centre of a field of force gravitational in type if not in kind. Surrounding atoms are attracted to the surface of a larger atom in number (the **Co-ordination Number**) sufficient to form an enclosing shell of atoms, which might or might not be identical in number with the numerical value of the valency of the central atom. Werner's theory was originally applied to the explanation of the valency of carbon, but, in 1893, he extended the theory to inorganic chemis-

<sup>1</sup> *Beiträge zur Theorie der Affinität und Valenz*, 1891

try,<sup>1</sup> and his "Co-ordination Theory" has found extensive application in nearly every field of theoretical and practical chemistry. Werner was not a mere theorist, for every point in his theory, accessible to experimental verification, was subjected to the most rigid examination. As Professor G. T. Morgan has stated, in his obituary notice of Werner "*he spared himself no pains to confirm these preconceptions by reference to cognate facts, or, if these were lacking, by crucial laboratory tests. His prevision was so exact and well focussed that in the majority of cases it was confirmed by experiment . . . Werner's generalisation has all the attributes of scientific theory of first-rate importance. It is in close accordance with known facts, which it explains and summarises in a logical and comprehensive manner. It endows its exponents with the gift of prophesy, and many far-reaching predictions based on its simple hypotheses have been verified subsequently by direct experiment.*"

The following generalisations emerge from the manifold details of the work of Werner and his school:

(a) valency is the numerically integral measure of the capacity of an atom for combination with hydrogen equivalents of atoms, being negative in combinations with electropositive atoms, and positive in combinations with electronegative atoms, and is therefore the measure of the extent of *reduction* or *oxidation* of an atom,

(b) chemical affinity is the attractive force brought into existence on atoms by operation of valency exchange, and attracts and binds atoms whether or not concerned in the valency exchange, that portion of the distributed force not utilised in binding atoms concerned in the valency exchange is termed **Residual Affinity**, which, though of the same electrical polarity as valency, is measurable, not in terms of hydrogen equivalents, but in terms of the number of atoms directly so bound;

<sup>1</sup> *Zeit anorg Chem*, 1893, 3, 267, 294, 310, *Lehrbuch der Stereochemie*, 1904 *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Brunswick, 1909 and 1909, *New Ideas on Inorganic Chemistry*, London, 1911

<sup>2</sup> *J Chem Soc*, 1920, 117, 1639

(c) atoms bound to a central atom in virtue of valency or residual affinity may or may not dissociate from the central atom on solution of the compound in solvents ;

(d) atoms, or groups of atoms united to a central atom through the medium of one of their atoms, can dissociate from a central atom to give rise to electrically charged ions only when such atoms, or groups, owe their combination to their valency ;

(e) the maximum number of electrically charged univalent ions, having polarity opposite to that of a central atom, that can dissociate from a central atom, is equal to the valency of the central atom ;

(f) the number of atoms, or groups of atoms, non-ionisably associated with a central atom, is the **Co-ordination Number** of the atom ;

(g) the maximum number of univalent ions of the same polarity as that of a central atom that can dissociate from a central atom is equal to the sum of the valencies of all the atoms attached other than by valency, and is usually equal to the difference between the co-ordination number and the valency of the central atom ;

(h) the intensity of the forces of attachment of co-ordinated atoms is a function of the valency of the co-ordinating atom, of the atomic volumes of the co-ordinated and co-ordinating atoms, and of temperature ;

(i) the co-ordination number is usually a constant, but may be variable, and a function of atomic volumes and temperature ;

(j) co-ordinated multivalent atoms may be simultaneously the co-ordinating atoms of subsidiary co-ordination complexes, which may have ions associated therewith in addition to the ions associated with the main co-ordination complex ;

(k) ionic dissociation of a co-ordination complex, not decomposed in solution, is possible only when the atoms combined exceed the co-ordination number ; if the number of atoms combined be less than the co-ordination number

the latter may be attained by addition of molecules of the solvent, and any ions resulting may be derived from the original compound or from the added solvent molecules; but the number of univalent ions, not including the complex ion, and not derived from subsidiary co-ordination complexes, cannot exceed the valency of the central atom.

(*l*) co-ordination compounds may be decomposed in solution and some or all of the co-ordinated atoms replaced by molecules of the solvent, such decomposition depending on the relative intensities of the residual affinities of the co-ordinated atoms and the reactive atoms of the solvent molecules,

(*m*) a multivalent atom or group, co-ordinated to a central atom in virtue of valency, can yield the complete multivalent ion only on replacement by a molecule of the solvent, unco-ordinated valences of a multivalent atom or group may be associated ionisably or otherwise with other atoms or with the co-ordination complex, a multivalent atom, or group, co-ordinated with a central atom by one valence and associated with the central atom by an unco-ordinated valence, is a **bound ion**;

(*n*) a group of atoms may be co-ordinated to a central atom by means of two of its atoms, the group thus occupying two co-ordination positions; such doubly co-ordinated groups may be bound by two valences, by one valence and residual affinity, or by residual affinity alone;

(*o*) co-ordinated atoms are arranged *in space* round the central co-ordinating (nuclear) atom with the **symmetry** of one or other of the **five regular solids**, each co-ordinated atom occupying one corner of the *imaginary* regular solid,

(*p*) **isomeric forms** of a co-ordination complex are possible according to the symmetry of the imaginary solid from which they are derived and according to the nature of the co-ordinated atoms;

(*q*) isomeric forms of co-ordination complexes are **optically active** when the complex does not contain a *centre*,

*plane*, or an *alternating axis* of symmetry, and optically active isomers exist in pairs which are related to one another as *object* and *non-superposable mirror-image* ;

(1) equal amounts of each of two oppositely optically active isomers of a co-ordination compound may give rise in the solid state to a racemic compound, and such a compound may be resolved into its generators by spontaneous crystallisation or by combination with another optically active compound ,

(2) apart from the capacity of atoms co-ordinated by valency to become charged ions on replacement by solvent molecules, *no difference* is detectable between the properties of atoms co-ordinated by valency and those of atoms co-ordinated by residual affinity.

The foregoing generalisations do not constitute an exhaustive presentation of the conclusions derived from the Co-ordination Theory, but suffice to present its broad outlines. Only a partial statement of the evidence relative to these generalisations can be given here, and the reader is referred for fuller details to Werner's publications and to Thomas' recent book on *Complex Salts*.

Though Werner's theory in its origin was entirely non-electrical, it was early obvious that his views on valency as against residual affinity were scarcely more precise than those of the founders of the valency theory. Werner, however, distinguished clearly that the bringing of valency into operation was not the immediate cause of the continued existence of chemical compounds, but merely a process of exchange between atoms which resulted in the creation of the actual forces causing and maintaining combination. Eventually he identified the exchange process of valency as the transfer of electrons from one to another atom to or from other atoms, the number of electrons transferred or acquired being the integral measure of valency, this transfer or acquiescence of electrons resulting in the creation of electric charges, recognisable only on ions formed in solutions. He identified chemical affinity with

the attractive force centred on an atom, and resulting from the electron transfer, residual affinity being that portion of the force not utilised in binding atoms concerned in the electron transfer. He postulated no definite mechanism by which atoms bound in a co-ordination complex became incapable of ionisation without further chemical reaction occurring.

The existence and persistence of the co-ordination complex was the central hypothesis of Werner's theory, but a masterly series of researches extending over thirty years conclusively demonstrated the reality of the three-dimensional co-ordination complex in highly diversified types of complex chemical compounds, and his central postulate is to-day no longer a hypothesis but a verified law of chemical combination.

The types of compounds, to which Werner's theory has been most widely applied, are the complex salts of metals and hydrogen with acidic atoms or groups such as the halogens, oxygen, sulphur, nitrogen, carbon, and boron and the oxy- and thio- acid radicals. Examples of these types are  $\text{HF.BF}_3$ ;  $\text{HCl.NH}_3$ ;  $\text{AlF}_3.3\text{NaF}$ ;  $\text{PtCl}_4.2\text{KCl}$ ;  $\text{CrCl}_3.6\text{H}_2\text{O}$ ;  $\text{CuCl}_2.3\text{CuO}.3\text{H}_2\text{O}$ ;  $\text{Sb}_2\text{S}_5.3\text{Na}_2\text{S}$ ;  $\text{BF}_3.\text{NH}_3$ ;  $\text{CoCl}_3.6\text{NH}_3$ ;  $\text{Co}_2\text{O}_3.\text{Cl}_2\text{Br}_2.8\text{NH}_3.\text{H}_2\text{O}$ ;  $\text{Co}_2\text{O}_3.2\text{CoBr}_3.6\text{H}_2\text{O}.12\text{NH}_3$ ;  $\text{Fe(CN)}_2.\text{CO}.3\text{KCN}$ ;  $\text{B(CH}_3)_3.\text{NH}_3$ ;  $\text{AlCl}_3.\text{H}_2\text{S}$ ;  $\text{AlBr}_3.3\text{C}_6\text{H}_6$ ;  $\text{CoCO}_3.\text{NO}_3.5\text{NH}_3$ .

In order to symbolise the fact of the integrity of the co-ordination complex Werner adopted the symbol of *square brackets* to enclose the formula of the complex, a method of symbolisation long in use for the partition of formulæ into radicals or compound ions. The co-ordination formulæ for the foregoing compounds thus become  $[\text{BF}_4]\text{H}$ ;  $[\text{NH}_4]\text{Cl}$ ;  $[\text{AlF}_6]\text{Na}_3$ ;  $[\text{PtCl}_6]\text{K}_2$ ;  $[\text{Cl}(\text{H}_2\text{O})_6]\text{Cl}_3$ ;  $[\text{Cu}(\text{OHCu}(\text{OH}))_3]\text{Cl}_2$ ;  $[\text{SbS}_4]\text{Na}_3$ ;  $[\text{BF}_3.\text{NH}_3]$ ;  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ;  $[\text{CoOH}.\text{Cl}(\text{NH}_3)_4]\text{Br}$ ,  $[\text{Co}\{\text{OHC}(\text{OH})(\text{NH}_3)_4\}_3]\text{Br}_6$ ,

$[\text{FeCO}(\text{CN})_5]\text{K}_3$ ,  $[\text{B}(\text{CH}_3)_3\text{NH}_3]$ ;  $[\text{AlCl}_3.\text{SH}_2]$ ,  
 $[\text{AlBr}(\text{C}_6\text{H}_5)_3]\text{Br}_2$ ; and  $[\text{CoCO}_3(\text{NH}_3)_5]\text{NO}_3$

Inspection of these formulæ shows that their predominant feature is the presence of four or six atoms or groups associated with a central atom, metallic or electro-positive in nature with the exception of the nitrogen atom in  $[\text{NH}_4]\text{Cl}$ . Examination of the many thousands of co-ordination compounds now known reveals the facts that the predominant co-ordination number is 6, and that the next most common number is 4, usually associated with the elements of small atomic weight such as Li, Be, B, C, and N, or elements of very large atomic weight such as Au, Hg, Tl, and Bi.

The progressive ionisation of co-ordination compounds by replacement of co-ordinated atoms or groups by molecules of a solvent (hydrolysis) is well illustrated by the triammine of cobaltic chloride  $[\text{CoCl}_3(\text{NH}_3)_3]$ . On solution of this compound in ice-cold water, ions are not at first detectable. On standing, one-third of the chlorine atoms become ionised, and the mono-hydrate, aquo-triamminocobaltic chloride,  $[\text{CoCl}_2\text{H}_2\text{O}(\text{NH}_3)_3]\text{Cl}$ , can be isolated from the solution. On long standing, two-thirds of the chlorine atoms become ionised, and the dihydrate, diaquo-triamminocobaltic chloride,  $[\text{CoCl}(\text{H}_2\text{O})_2(\text{NH}_3)_3]\text{Cl}_2$ , can be isolated from the solution. On raising the temperature, the whole of the chlorine atoms become ionised and the trihydrate, tri-aquo-triamminocobaltic chloride,  $[\text{Co}(\text{H}_2\text{O})_3(\text{NH}_3)_3]\text{Cl}_3$ , can be isolated.

The three molecules of ammonia can not be progressively removed by replacement by the solvent owing to the instability of the resulting hydrates. The reverse process of replacement of the water molecules can however be accomplished, either by substitution by atoms previously ions or by replacement (ammonolysis) by further ammonia molecules, the following series of compounds being obtainable by treatment with ammonia, diaquo-tetrammino-

cobaltic chloride,  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_3$ , aquo-pentamino-cobaltic chloride,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3$ , and hexammino-cobaltic chloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ .

The complete series of compounds containing chlorine atoms and water or ammonia molecules in the co-ordination complex is also obtainable, tetrammino-cobaltic chloride,  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ , aquo-tetrammino-cobaltic chloride,  $[\text{CoCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$ , and pentammino-cobaltic chloride,  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ . All of the foregoing ten compounds can be arranged into *four types*, according to the number of acidic atoms in the co-ordination complex, tri-acido-type,  $[\text{CoX}_3\text{A}_3]$ , diacido-type,  $[\text{CoX}_2\text{A}_4]$ , mono-acido-type,  $[\text{CoXA}_5]$ , and the non-acido-type,  $[\text{CoA}_6]$ , "X" being a univalent acidic atom or monobasic acid radical, and "A" any molecule containing one atom with residual affinity for electronegative type.

No other types of acido-co-ordination complexes are possible with co-ordination number 6 and a trivalent central atom, though it is customary to regard complexes such as  $[\text{Co}(\text{NO}_2)_6]$ ,  $[\text{Co}(\text{NO}_2)_5\text{NH}_3]$ , and  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$  as separate types. They are however merely variants of the tri-acido-type, in which three molecules of ammonia are replaced by three molecules of a simple salt such as sodium nitrite,  $\text{NaNO}_2$ , the complexes thus being associated with three ions, two ions, and one ion of a univalent metal or basic group, the compounds thus having the formulæ  $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$ ,  $[\text{Co}(\text{NO}_2)_5\text{NH}_3]\text{Na}_2$ , and  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]\text{Na}$ .

The fact that the three, two, and one molecules of the added salt are capable of independent ionisation follows from the circumstance that only one of the two atoms of each added molecule is bound in the co-ordination complex. The hydrogen atoms of ammonia are co-ordinated to nitrogen and co-ordinated ammonia molecules consequently furnish no hydrogen ions. Molecules of co-ordinated water, however, almost invariably furnish hydrogen ions, and the aquo-salts are consequently always acid

in reaction. The compound,  $[\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}]\text{Cl}_3$ , known as roseo-cobalt chloride, or aquo-pentammino-cobaltic chloride, can in fact be titrated with alkalis in precisely the same way as a mono-basic acid, and the result of neutralisation (or hydrolysis) is the basic salt,  $[\text{Co}(\text{NH}_3)_5 \cdot \text{OH}]\text{Cl}_2$ , known as basic-purpureo-cobalt chloride, or hydroxo-pentammino-cobaltic chloride.

In order to indicate the fact that the hydroxide not a chloride radical is bound non-ionisably in the co-ordination complex, Werner adopted the nomenclature used in similar cases in organic chemistry, the acidic atom substituted in a "*nucleus*" being given the suffix "*o*," for example chloro-methyl-cyanide,  $\text{ClCH}_2-\text{CN}$ , bromo-acetyl-chloride,  $\text{BrCH}_2-\text{COCl}$ , and nitro-benzoic acid,  $\text{NO}_2\text{C}_6\text{H}_4-\text{COOH}$ . Hence the use of such names as chloro-pentammino-cobaltic chloride for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , and hydroxo-aquo-tetrammino-cobaltic chloride for  $\text{Co}[(\text{NH}_3)_4 \cdot \text{H}_2\text{O} \cdot \text{OH}]\text{Cl}_2$ .

However useful this nomenclature may be for these classes of compounds, it fails when applied to the tri-acido-type of co-ordination compounds.  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ , for example, must become trichloro-triammino-cobaltic. To obviate this, Werner was driven to regard the cobalt as acting acidically, and called the compound trichloro-triammino-cobaltiate. This nomenclature is quite unnecessary, for the simple name triammino-cobaltic chloride conveys all that need be understood of the chemical nature of the compound. The old name potassium ferrocyanide,  $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$ , in Werner's system, becomes potassium hexacyano-ferroate,  $[\text{Fe}(\text{CN})_6]\text{K}_4$ . Werner's nomenclature is unfortunate in that it conveys nothing that the older and much simpler nomenclature does not convey, and he was frequently obliged to suppress the very facts that his nomenclature was invented to provide for, the ionisation of parts of a complex. Strictly his name aquo-pentammino-cobaltic chloride should be hydroxo-pentammino-cobaltic dichloride hydrochloride, for the aquo-group furnishes a hydrogen ion in solutions.

Methyl ferrocyanide,  $\text{Fe}(\text{CN})_2 \cdot 4\text{CH}_3\text{CN}$ , termed in Werner's system methyl hexacyano-ferriate, should be tricyano-tri-cyanomethyl-ferriate, for the four methyl cyanide molecules no more furnish methyl ions than ammonia molecules furnish hydrogen ions. The non-ionisation of the methyl groups explains the existence of the *two isomers*  $\alpha$ - and  $\beta$ -methyl ferrocyanides, as the *cis* and *trans* forms of an octahedral complex. It may be stated that any system of chemical nomenclature based on ionisation is bound to fail, for the simple reason that ionisation may have any value from infinitesimal to complete, depending on the solvent and the extent of dilution of the solution.

A stronger objection to Werner's nomenclature is the fact that it is not consistent with his co-ordination theory in which metallic amines are regarded as ammonium derivatives. If ammonium chloride is validly describable as the product of the addition of the electro-positive part of a simple salt, hydrogen chloride, to the electro-negative nitrogen of ammonia, then metallic amines are similar ammonium compounds, consisting of the product of the addition of the electro-positive part of a simple salt, cobaltic chloride, to the electro-negative nitrogen of ammonia.  $\text{CoCl}_3 \cdot 3\text{NH}_3$  is consequently cobaltic-tri-ammonium chloride, just as  $\text{CH}_3\text{Cl} \cdot \text{NH}_3$  is methylammonium chloride in organic chemistry. In the strict ammonium nomenclature  $\text{CoCl}_3 \cdot 3\text{NH}_4\text{Cl}$  would be ammonium cobaltic-chloride,  $\text{CoCl}_3 \cdot \text{NH}_3 \cdot 2\text{NH}_4\text{Cl}$  would be diammonium cobaltic-ammonium chloride, and  $\text{CoCl}_3 \cdot 2\text{NH}_3 \cdot \text{NH}_4\text{Cl}$  would be ammonium cobaltic-diammonium chloride.

Werner's use of the term ammino is a convenient shorthand form for co-ordinated ammonia, but no justification exists for the use of such terms as cobaltiate and ferriate, a method of nomenclature already in common use to designate oxy-acids. The confusion ensuing from Werner's nomenclature is illustrated by the fact that the common

oxy-salt potassium chloro-chromate,  $\text{KCrO}_3\text{Cl}$ , would scarcely be differentiated by name from the double salt,  $\text{CrCl}_3.3\text{KCl}$ , at present known as potassium chromichloride.

The foregoing three general types of co-ordination complexes derived from trivalent metals include those in which a single group of atoms contributes more than one to the six co-ordination positions, and numerous cases are known of *doubly-bound* groups, and at least one *trebly-bound* group has been identified by Werner.

Groups of the type of ethylenediamine,  $\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$ , and metallic hydroxides, e.g.  $\text{Cu}(\text{OH})_2$ , are equivalent to two molecules of ammonia. Groups of the type of the aminoacetate group,  $\text{NH}_2.\text{CH}_2.\text{CO}_2-$ , and the acetyl-acetone radical,  $\text{O}:\text{C}.\text{CH}:\text{C}.\text{O}-$ , are equivalent to one

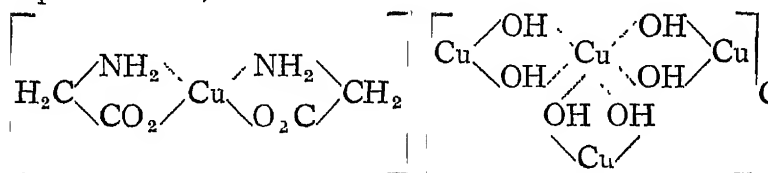


molecule of ammonia and one univalent atom. Groups of the type of the oxalate group,  $-\text{O}_2\text{C}.\text{CO}_2-$ , and the pentamethylene radical,  $-\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2-$ , are equivalent to two univalent atoms.

Professor G. T. Morgan has proposed to designate all groups, contributing *two* positions to a co-ordination complex, **Chelate Groups**. Complexes containing three of the first type of chelate group belong to the general non-acido-type,  $[\text{MA}_6]$ . Those containing one chelate group of the second type and four molecules of ammonia belong to the general mono-acido-type,  $[\text{MXA}_5]$ . Those containing two such chelate groups and two molecules of ammonia belong to the general di-acido-type,  $[\text{MX}_2\text{A}_4]$ . Those containing three such chelate groups belong to the general tri-acido-type,  $[\text{MX}_3\text{A}_3]$ . Complexes containing one chelate group of the third type and four molecules of ammonia belong to the general di-acido-type, while those containing two or three such chelate groups belong to the general tri-acido-type.

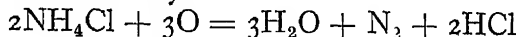
It is obvious that a chelate group by combination with a central atom gives rise to a *cyclic system*, for example,

$\text{Co} \begin{array}{c} \text{NH}_2 - \text{CH}_2 \\ | \\ \text{NH}_2 - \text{CH}_2 \end{array}$ . In cases where two or more chelate groups combine with a central atom, the latter becomes the common member or *spiro*-atom of two or more cyclic systems, for example, in cupric amino-acetate, and basic cupric chloride,

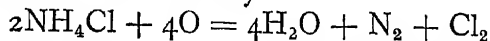


In the first case the valency of copper is expended in the co-ordination complex, whereas in the other the two chloride ions associated with the complex ion account for the valency of copper, the complex ion thus being a diacidic basic radical, in accordance with the rule that the maximum number of univalent ions associated with a complex is equal to the valency of the co-ordinating atom.

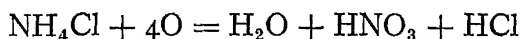
It was indicated, page 87, that ammonium chloride differed from the co-ordination compounds of metals in containing a central *electronegative* atom, its co-ordination formula being  $[\text{NH}_4]\text{Cl}$ . This compound may, however, be regarded as an ammine of electropositive hydrogen  $[\text{H}.\text{NH}_3]\text{Cl}$ , and is thus strictly analogous to a metallic ammine. Either method of formulation involves that the valency of nitrogen is unchanged in ammonia and ammonium salts. This can readily be demonstrated experimentally. On oxidation of ammonium chloride to water, free nitrogen and hydrochloric acid, only three equivalents of oxygen are necessary.



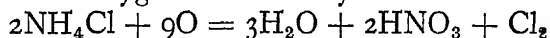
On oxidation to water, free nitrogen, and free chlorine, four equivalents are necessary.



On oxidation to water, nitric acid, and hydrochloric acid, eight equivalents are necessary.



On oxidation to water, nitric acid, and free chlorine, nine equivalents of oxygen are necessary.



If ammonium chloride contained quinquevalent nitrogen the equivalents of oxygen necessary for these oxidations would be increased by two in all cases. If the nitrogen atom were electropositively quinquevalent as in nitric acid, then no oxidation would be necessary, and hydrolysis alone would yield nitric acid, hydrogen, and hydrochloric acid. Ammonium chloride, however, on complete hydrolysis yields only ammonia and hydrochloric acid.

It must therefore be concluded that ammonium salts contain not merely *trivalent* nitrogen but *electronegative nitrogen*, and that the nitrogen atom is completely reduced just as is the oxygen atom in water and the chlorine atom in hydrochloric acid. It may thus be inferred that the nitrogen atom in ammine combinations is equivalent in type of affinity to oxygen, chlorine, and other acidic atoms, and that the metallic atoms of co-ordination complexes possess electropositive valency and electropositive residual affinity. Hence it is that the co-ordinated atoms in metallic co-ordination compounds are almost invariably nitrogen, oxygen, fluorine, chlorine, bromine, and iodine, and that metallic co-ordination compounds are usually amines, hydrates, complex oxy-salts, oxides, and double halides. Co-ordination compounds of the ammonium type, on the other hand, are usually hydrides or carbon compounds with non-metals.

The so-called boronium, thallonium, carbonium, siliconium, titanonium, stannonium, stibonium, bismuthonium, and iodonium compounds exhibit no real analogy to ammonium compounds, but contain as truly electropositive central atoms as do the metallic amines, and the same is probably true of many sulphonium, phosphonium, and arsonium compounds. Even the nitrogen atom, so frequently highly electronegative, becomes an electropositive

central atom in combination with oxygen and perhaps the halogen elements.

An interesting example of the direct combination of electropositive nitrogen with electronegative nitrogen, both in the trivalent state, may be regarded as furnished by one of the nitrogen iodides,  $N_2H_3I_3$ , to which the co-ordination formula  $[NI_3.NH_3]$  may be assigned, each nitrogen contributing one position of opposite polarity to the four co-ordination positions of the other. The reactions of the compound, however, indicate that this elegant formulation is doubtful, as nearly the whole of the nitrogen is evolved free on hydrolysis, and the compound reacts with moist ammonia to form  $NI_3.2NH_3$  and  $NI_3.3NH_3$ . It seems probable, therefore, that the nitrogen atom is electrically negative even in combination with the halogens, and that the nitrogen iodides contain electropositive iodine, the constitution of the last compound thus being  $[(NH_3.I)_3N]$  only three of the four electronegative nitrogen atoms attaining the co-ordination number four.

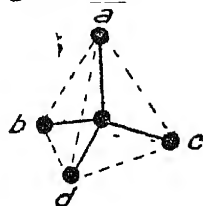
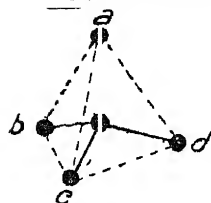
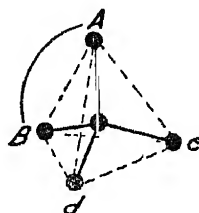
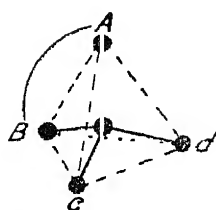
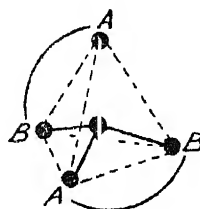
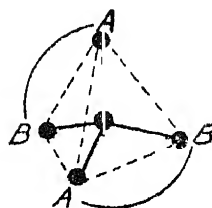
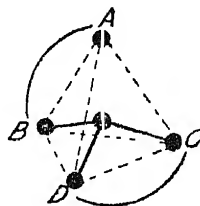
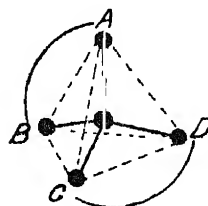
## CO-ORDINATION STEREO-CHEMISTRY

THE spatial distribution of the forces of chemical affinity consequent on valency exchange, necessarily involved in Werner's theory the spatial distribution of atoms about a central atom. The spatial distribution of atoms united to the quadrivalent carbon atom was the essential feature of the theories in organic chemistry associated with the names of van't Hoff and Le Bel, and Werner's co-ordination theory further extended stereo-chemical conceptions in organic chemistry and to inorganic chemistry generally. Werner postulated that all atoms with co-ordination number four possessed a tetrahedral configuration, and those with co-ordination number six an octahedral configuration.

It is extremely doubtful, however, that Werner's postulate is universally correct, for he was compelled to admit a planar distribution of co-ordination positions for the bivalent platinum atom with the co-ordination number four, though the six co-ordination positions of quadrivalent platinum were definitely demonstrated to be not only spatial but octahedral. It is more than possible that many atoms with co-ordination number four possess a planar distribution of valency forces. Vernon<sup>1</sup> has contributed considerable evidence for the planar distribution in the case of the dimethyl halides of bivalent tellurium, and Morgan and Drew and their co-workers have detected no stereoisomers in the case of the di-selenium acetylacetonates, though such should exist if the selenium atoms in these compounds have not a planar distribution of valency forces.

With regard to atoms having the co-ordination number six, Werner was able to demonstrate their octahedral structure in all the cases examined, and until recently it appeared that his generalisation of octahedral structure for six co-ordination positions was correct in all cases. The triacetylacetonates of the trivalent metals however, should exist in two optically active forms, and, though no evidence

<sup>1</sup> *J. Chem. Soc.*, 1920, 117, 86, 889, 119, 105, and 687

Tetrahedral Optical IsomersClass 1(v) without Chelate GroupsClass 2(iv) with one unsymmetrical Chelate GroupClass 3(iv) with two similar unsymmetrical Chelate GroupsClass 3(v) with two dissimilar unsymmetrical Chelate Groups

has been obtained to this effect, it has been assumed that the known compounds are merely unresolved racemic compounds.

The researches of Mr. W. T. Astbury, however, prove that this explanation is untenable. His examination of numerous triacetylacetones by crystallographic and X-ray analysis indicates that the octahedral structure is impossible, and that the spatial arrangement is that of the trigonal prism. This deduction in no way affects the reality of the octahedral structures assigned by Werner to chromium, iron, cobalt, rhodium, iridium, and platinum atoms as the result of his chemical investigations. It merely proves that

TABLE 4

Number of	CHELATE GROUPS		
	None	One	Two
Type	1	2	3
Class (i)	aaaa	AA bb	AA AA
(ii)	aaab	AB cc	AA BB
(iii)	aabb	AA bc	AA BC
(iv)	aabc	AB cd*	AB AB*
(v)	abcd*	—	AB CD*

\* Represents two optically active isomers

the octahedron is not the invariable six-point structure for these and other atoms. The new evidence indicates that the regular octahedron and the trigonal prism are limiting types of atomic six-point structure, and that Werner erred only in a too-inclusive formulation of his postulate as to spatial distribution of co-ordination positions. The importance of Werner's contribution to the theory of molecular and atomic structure is not thereby materially affected.

Examination of the symmetry of the tetrahedron indicates that tetrahedral co-ordination complexes may be

classified into three main types and fourteen classes according to the number of chelate groups associated with the central atom. Representing a co-ordinated chelate group by two capital letters to symbolise its symmetrical or unsymmetrical nature, and atoms or groups, occupying only one co-ordination position, by small letters, the three types and fourteen classes of tetrahedral co-ordination complexes are shown in Table 4, page 97.

Of these fourteen classes only 1 (v), 2 (iv), 3 (iv), and 3 (v) represent two isomeric complexes, i.e. complexes related to one another as object and non-superposable mirror-image, and at least one of these complexes must be present in any compound exhibiting optical activity. The eight optically active complexes, in four mirror-image pairs are shown in Diagram III, p. 96. The first three optically active classes have been demonstrated to exist, though the two isomeric compounds of the 3 (iv) class (symmetrical spiro-nucleus) have only recently been obtained for the first time by Mills and Nodder<sup>1</sup> by the optical resolution of the racemic ortho-dilactone of benzophenone tetracarboxylic acid. As yet no compounds of the 3 (v) class (asymmetric spiro-nucleus) have been obtained optically active, though little doubt can be thrown on their possible existence. The fact that thirteen of the fourteen possible classes have been proved to exist and to give rise to the theoretical number of isomers renders impossible any other than the tetrahedral nature of the quadrivalent carbon atom.

Some of the foregoing optically active classes have been proved to exist containing nitrogen, sulphur, tin, silicon, phosphorus, arsenic and selenium as co-ordinating atoms and the tetrahedral nature of these atoms is therefore (see p. 46) certain. Most of the optically inactive classes have been proved to exist containing lithium, beryllium, boron, oxygen, chlorine, bromine, iodine, gold, mercury, thallium, and bismuth, and the tetrahedral nature of these

<sup>1</sup> *J. Chem. Soc.*, 1921, 119, 2094

atoms is scarcely less certain than in the cases of the foregoing.

The foregoing three types and fourteen classes of tetrahedral co-ordination complexes relate only to uni-nuclear compounds, i.e. those containing one central atom, but all compounds containing any number of central co-ordinating atoms are simply derivable from these types and classes by combination. As no tetrahedral nuclear atom regarded separately can give rise to more than two isomeric forms, both of which are equally and oppositely optically active, two such nuclear atoms cannot give rise to more than  $2 \times 2 = 4$  binuclear isomers, three nuclear atoms to no more than  $2 \times 2 \times 2 = 8$  trinuclear isomers, four to no more than  $2 \times 2 \times 2 \times 2 = 16$  quadrinuclear isomers, and in general  $n$  central atoms to no more than  $2^n$  multinuclear isomers.

If two similar nuclear atoms are situated symmetrically in a chain of atoms, the chain can be divided into two equal portions each containing one of the nuclear atoms. One uninuclear half-chain is capable of existing in two isomeric forms, and each of these forms is identical with an isomeric form of the other half-chain, or, in other words, the two uninuclear half-chains yield only two sorts of forms, related to one another as optical isomers. These two half-chains can be combined together to form a complete binuclear chain in three different ways, the first consisting of two identical half-chains of one sort, the second of two identical half-chains of the other sort, and the third of a half-chain of each sort. The first two binuclear chains are equally and oppositely optically active, and the third optically inactive. These three isomeric forms are the maximum number of isomers possible with two similar nuclear atoms symmetrically situated in a chain of atoms.

Such inactive forms are described in organic chemistry as *meso*-forms, and are said to be inactive by *internal compensation*, meaning thereby that the half-molecules, of which they may be regarded as composed, are equally and

oppositely optically active and consequently reduce the activity of the whole molecules to zero

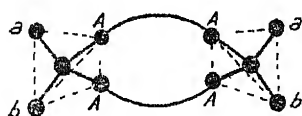
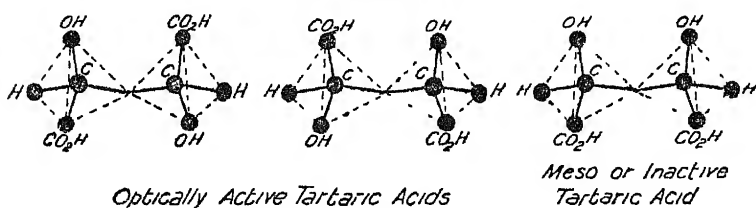
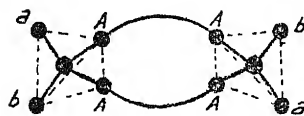
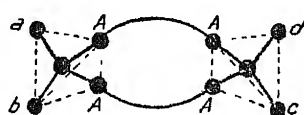
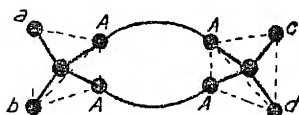
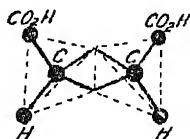
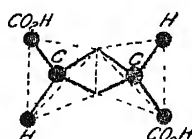
It is obvious that the number of meso-forms corresponding to any formula must be equal to half the number of optical isomers, that is, equal to the number of pairs of such isomers. (Optical isomers are usually described as *enantiomorphs*, or enantiomorphic pairs.) Meso-forms can only exist when a formula can be divided into two equal portions, and, in general, meso-forms are equal in number to one quarter of the number of isomers theoretically derivable from the total number of nuclear atoms in the formula. The number of corresponding optically active isomers is equal to one-half the theoretical total number of isomers. If the number of nuclear atoms, capable of giving rise to isomers, be  $n$  and the formula be symmetrical, the number of enantiomorphs is equal to one-half of  $2^n$ ,  $= 2^{n-1}$ . As the number of meso-forms is one-half of the number of enantiomorphs, the number of meso-forms is one-half of  $2^{n-1}$ ,  $= 2^{n-2}$ , and the total number of isomers, optically active and inactive, is thus equal to  $3 \times 2^{n-2}$ .

The simplest case of two nuclear atoms, symmetrically situated in a chain of atoms, is illustrated by the three isomeric tartaric acids shown in Diagram IV, two of these isomers being enantiomorphs and the other an inactive or meso-form. It is usual to add to these three forms a fourth form known as racemic acid, a compound of equal numbers of molecules of the two enantiomorphic isomers. Strictly, racemic tartaric acid is not an isomeric tartaric acid, for its molecular weight, were it ascertainable, must be at least double that of any of the three truly isomeric tartaric acids. Racemic compounds do not owe their existence to different arrangements of the atoms in molecules, but to combination between two different molecules which are enantiomorphs, the number of racemic forms thus being inevitably equal to the number of enantiomorphic pairs of isomers.

A special type of isomerism arises in the case of com-

pounds containing two nuclear atoms, each of the symmetrical mono-chelate class 2 (iii), when the chelate group is common to both nuclei, and each nucleus is symmetrically

DIAGRAM IV

*Cis Form**Trans Form**Isomers of**Two Similar Tetrahedral Systems with one Chelate Group in Common**Cis and Trans Isomers of**Two Dissimilar Tetrahedral Systems with one Chelate Group in Common**Cis Form  
Maleic Acid**Trans Form  
Fumaric Acid*

situated in the chelate group of the other. Owing to the fact that class 2 (iii) involves the nuclear atom being attached to two unlike atoms or groups, the chelate group can be applied in two different ways to the nuclear atom,

the two dissimilar atoms in the nucleus in the chelate group in one case being reversed in "orientation" (relative position in space). If the two nuclei are identical, these two positions correspond to bringing similar atoms on the same side of the molecule, called the *cis* position, or on opposite sides of the molecule, called the *trans* position. If the two nuclei are not identical, the terms *cis* and *trans* can be applied only arbitrarily. The two cases are illustrated in Diagram IV, page 101.

As the nuclear atoms belong to class 2 (iii), each nuclear system must separately contain a plane of symmetry, and as the symmetrical chelate group is common to both systems, the plane of symmetry must be identical for both nuclear systems. As complexes containing a plane of symmetry cannot be optically active, *cis* and *trans* isomers cannot be optically active, unless another nuclear atom is present belonging to one of the classes 1 (v), 2 (iv), 3 (iv), and 3 (v), in which event there would exist at most four isomers, two *cis*-enantiomorphs and two *trans*-enantiomorphs. Numerous cases are known in the cyclic structures of organic chemistry.

The limiting cases of the *cis* and *trans* type of isomerism is reached when the chelate group is reduced to one atom, the isomers then consisting of two nuclear atoms united by a double-bond. This is the most familiar case of *cis* and *trans* isomerism in organic chemistry, and includes open-chain and cyclic ethylene derivatives, oximes, hydrazones, and diazonium compounds. The ethylene type of isomerism in maleic acid and fumaric acid is illustrated in Diagram IV, page 101.

In organic chemistry it is usual to refer to an atom, such as a carbon atom, as an *asymmetric* atom, when, acting as a nuclear atom of a tetrahedral system, it is so combined as to give rise to optical isomers or enantiomorphs. This term, due to van't Hoff, has no justification on the chemical evidence, for phenomena of optical activity can arise even if the carbon atom be as perfectly symmetrical as the

regular tetrahedron. The only asymmetry that has ever been detected in chemistry is the asymmetry of molecules as a whole, such asymmetry arising merely from the spatial distribution of atoms or groups about a central atom, which may itself have any symmetry elements whatever. There is in fact good reason to suppose that the carbon atom in all of its combinations possesses at least one of the six planes of tetrahedral symmetry.

The symmetry of the octahedron is much more complex than that of the tetrahedron, and octahedral co-ordination complexes are consequently much more varied in type. Four main types are possible according to the number of chelate groups united to the central atom, the first type being non-chelate, the second mono-chelate, the third di-chelate, and the fourth tri-chelate.

These groups may be further divided into forty-one classes, eleven of the non-chelate type, and ten each of the three chelate types. The eleven non-chelate classes give rise to seventy-five forms, of which fifty are optically active. The ten classes of the mono-chelate type give rise to seventy-two forms, of which fifty-eight are optically active. The ten classes of the di-chelate type give rise to eighty forms, of which seventy are optically active. The ten classes of the tri-chelate type give rise to fifty-four forms, all of which are optically active. The octahedral configuration thus gives rise to two hundred and eighty-one forms, of which two hundred and thirty-two are optically active in one hundred and sixteen enantiomorphous pairs. The following tables 5, 6, 7, 8, and 9, detail the various classes and forms.

Of the forty-one classes of octahedral complexes, twenty-two have been experimentally realised, the first nine of type 1, the first five of types 2 and 3, and the first two and the fourth of type 4. None of the classes of type 1 have yet been obtained in optically active forms, but the inactive forms correspond to the theoretical number in nearly all cases.

None of type 2 had been obtained in optically active

TABLE 5.—TYPES AND CLASSES OF OCTAHEDRAL SYMMETRY

Number of Type	CHELATE GROUPS			
	None 1	One 2	Two 3	Three 4
Class (i)	aaaaaa	AA bbbb	AA AA bb	AA AA AA
(ii)	aaaaab	AB cccc	AA BB cc	AA AA BB
(iii)	aaaabb	AA bbbc	AA AA bc	AA BB CC
(iv)	aaaabc	AB cccd	AA BB cd	AA AA CD
(v)	aaabbb	AA bbcc	AA BC dd	AA BB CD
(vi)	aaabbc	AB ccdd	AB AB cc	AB AB AB
(vii)	aaabcd	AA bbcd	AB CD ee	AA BC BC
(viii)	aabbcc	AB ccde	AB AB cd	AA BC DE
(ix)	aabbcd	AA bcde	AA BC de	AB AB CD
(x)	aabcde	AB cdef	AB CD ef	AB CD EF
(xi)	abcdef	—	—	—

TABLE 6.—ISOMERIC CLASSES AND FORMS OF NON-CHELATE TYPE I

Classes	NUMBER OF ISOMERIC FORMS									
	Optically Active				Optically Inactive					
	Cis	Trans	Other	Total	Cis	Trans	Other	Total	Total	
(i)	—	—	—	—	—	—	1	1	1	
(ii)	—	—	—	—	—	—	1	1	1	
(iii)	—	—	—	—	1	1	—	2	2	
(iv)	—	—	—	—	1	1	—	2	2	
(v)	—	—	—	—	1	1	—	2	2	
(vi)	—	—	—	—	1	2	—	3	3	
(vii)	2	—	—	2	—	3	—	3	5	
(viii)	2	—	—	2	—	4	—	4	6	
(ix)	4	—	—	4	—	4	—	4	8	
(x)	12	—	—	12	—	3	—	3	15	
(xi)	—	—	30	30	—	—	—	—	30	
Total	20	Nil	30	50	4	19	2	25	75	

TABLE 7.—CLASSES AND ISOMERIC FORMS OF  
MONO-CHELATE TYPE 2

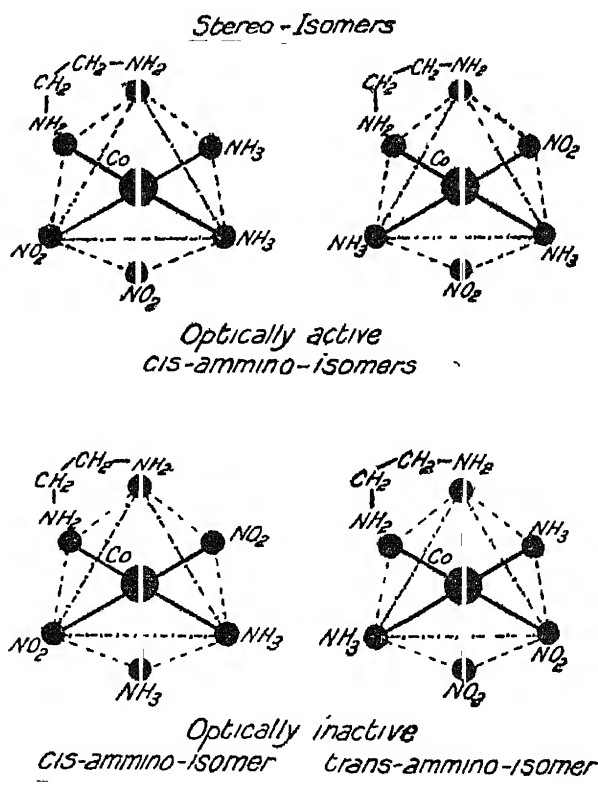
Classes	NUMBER OF ISOMERIC FORMS								
	Optically Active				Optically Inactive				
	Cis	Trans	Other	Total	Cis	Trans	Other	Total	Total
(I)	—	—	—	—	—	—	1	1	1
(II)	—	—	—	—	—	—	1	1	1
(III)	—	—	—	—	1	1	—	2	2
(IV)	2	—	—	2	—	2	—	2	4
(V)	2	—	—	2	—	2	—	2	4
(VI)	4	—	—	4	—	2	—	2	6
(VII)	4	—	—	4	—	2	—	2	6
(VIII)	10	—	—	10	—	2	—	2	12
(IX)	—	—	12	12	—	—	—	—	12
(X)	—	—	24	24	—	—	—	—	24
Total	22	Nil	36	58	1	11	2	14	72

TABLE 8.—CLASSES AND ISOMERIC FORMS OF  
DI-CHELATE TYPE 3

Classes	NUMBER OF ISOMERIC FORMS								
	Optically Active				Optically Inactive				
	Cis	Trans	Other	Total	Cis	Trans	Other	Total	Total
(I)	2	—	—	2	—	1	—	1	3
(II)	2	—	—	2	—	1	—	1	3
(III)	2	—	—	2	—	1	—	1	3
(IV)	4	—	—	4	—	1	—	1	5
(V)	4	—	—	4	—	1	—	1	5
(VI)	2	4	—	6	—	2	—	2	8
(VII)	8	—	—	8	—	2	—	2	10
(VIII)	4	6	—	10	—	1	—	1	11
(IX)	8	4	—	12	—	—	—	—	12
(X)	16	4	—	20	—	—	—	—	20
Total	52	18	Nil	70	Nil	10	Nil	10	80

forms, until Thomas<sup>1</sup> in 1923 obtained the cis-dinitro-oxalato-diammino-cobaltic complex, of class 2 (v) in two optically active and one trans-dinitro-inactive form,

DIAGRAM V



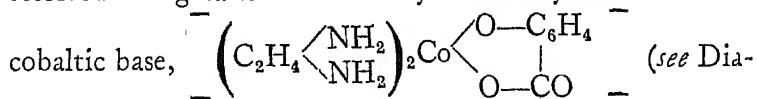
being three of the four theoretically possible cis and trans isomeric forms of this class. The correct number of isomers has been obtained for classes (i), (ii), (iii), and (v) of type 3, by Werner, but the optically active isomers of class 3 (iv) have not yet been obtained. Werner was also

<sup>1</sup> *J Chem Soc*, 1923, 123, 617

TABLE 9.—CLASSES AND ISOMERIC FORMS OF TRI-CHELATE TYPE 4

Classes	NUMBER OF ISOMERIC FORMS								
	Optically Active				Optically Inactive				Total
	Cis.	Trans	Other	Total	Cis.	Trans	Other	Total	
(i)	—	—	2	2	—	—	—	—	2
(ii)	—	—	2	2	—	—	—	—	2
(iii)	—	—	2	2	—	—	—	—	2
(iv)	—	—	2	2	—	—	—	—	2
(v)	—	—	4	4	—	—	—	—	4
(vi)	2	2	—	4	—	—	—	—	4
(vii)	2	4	—	6	—	—	—	—	6
(viii)	—	—	8	8	—	—	—	—	8
(ix)	4	4	—	8	—	—	—	—	8
(x)	—	—	16	16	—	—	—	—	16
Total	8	10	36	54	Nil	Nil	Nil	Nil	54

successful in obtaining the correct number of isomers for several representatives of classes 4 (i), 4 (ii), and 4 (iv), but in the case of the last class Werner was unable to resolve into the optical isomers the racemic compounds containing only one nuclear atom, which were however obtained by synthesis from optically active compounds. Racemic compounds of this class, with only one nuclear atom, have only this year been resolved by Morgan and Main Smith<sup>1</sup> into the correct number of optical isomers, the compounds resolved being salts of the salicylato-diethylenediamminocobaltic base,

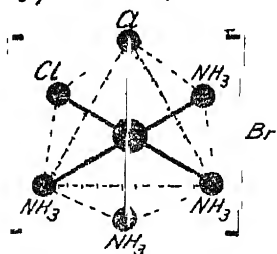
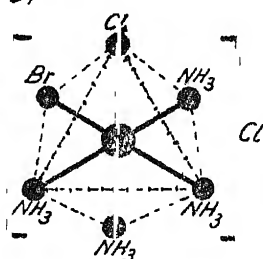
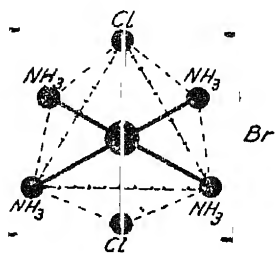
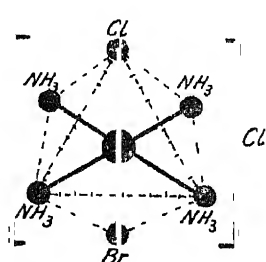


The great majority of the foregoing classes actually known are complexes containing the cobalt atom as the central co-ordinating atom, but many of the classes are also known containing chromium, iron, rhodium, and iridium as

<sup>1</sup> *J Chem Soc*, 1924, 125

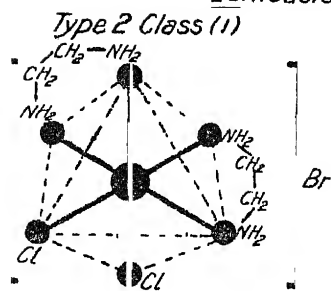
nuclear atoms, and all of them have been proved to give rise to optically active isomeric forms. These atoms have therefore quite definitely a six-point spatial structure, which is octahedral.

DIAGRAM VI

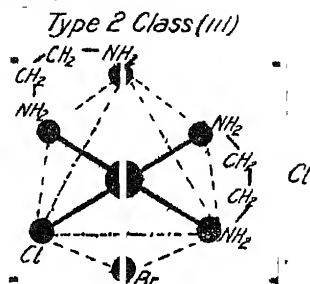
*Ionisation Isomers**Type I Class (III)**Bromide of  
cis-di-chloro-isomer**Type I Class (IV)**Chloride of  
cis-chloro-bromo-isomer**Bromide of  
trans-di-chloro-isomer**Chloride of  
trans-chloro-bromo-isomer**Di-acido-tetrammino-cobaltic halides*

Though no optically active isomers are known in the cases of magnesium, aluminium, silicon, phosphorus, sulphur, scandium, titanium, vanadium, manganese, nickel, copper, zinc, gallium, germanium, selenium, yttrium, zirconium, columbium, molybdenum, ruthenium, palla-

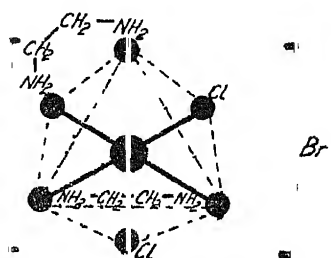
## DIAGRAM VII

*Ionisation Isomers*

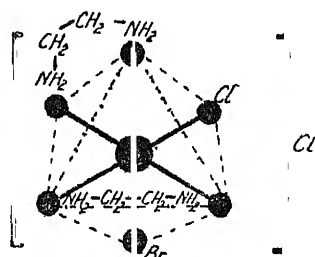
*Optically active bromide of  
cis-di-chloro-isomer*



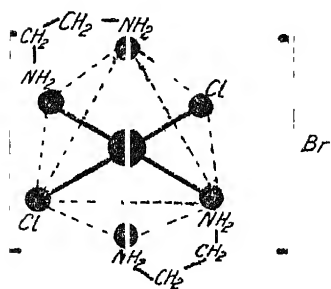
*Optically active chloride of  
cis-chloro-bromo-isomer*



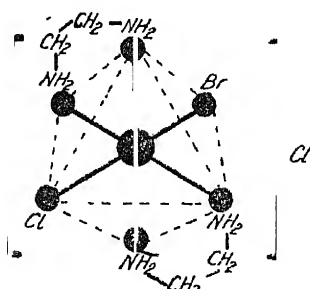
*Optically active bromide of  
cis-di-chloro-isomer*



*Optically active chloride of  
cis-chloro-bromo-isomer*



*Optically inactive bromide of  
trans-di-chloro-isomer*



*Optically inactive chloride of  
trans-chloro-bromo-isomer*

*Di-amido-diethylenediamino-cobaltic halides*

dium, silver, cadmium, indium, tin, antimony, tellurium, lanthanum and the rare earth metals, cerium, tantalum, tungsten, osmium, platinum, lead, thorium, and uranium. A sufficiently large number of the inactive forms of many of the classes are known to render practically certain that these elements can possess a six-point spatial atomic structure, which is probably octahedral.

The foregoing forty-one classes of octahedral coordination complexes do not include the whole of the possible isomeric compounds, but represent only those derived from one coordination complex irrespective of the ions with which the complex may be associated. Many dozens of cases of isomeric compounds are known in which the isomerism is a consequence of the position of atoms or groups *in or ionically associated with* a complex ion; dichloro-tetrammino-cobaltic bromide,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ , for example, represents two isomers of class 1 (iii), the cis and trans forms of the complex ion, both of which are isomeric with the two corresponding isomers of class 1 (iv) of the complex ion of chloro-bromo-tetrammino-cobaltic chloride  $[\text{Co}(\text{NH}_3)_4\text{Cl.Br}]\text{Cl}$ . These pairs of isomers, *ionisation isomers*, derived from two different complex ions, are shown in Diagram VI, page 108.

If the four ammonia molecules be replaced by two molecules of ethylenediamine, the dichloro-bromide can exist in three isomeric forms, two cis and one trans, of class 2 (i) which are ionisation isomers of the corresponding three isomers of class 2 (iii) of the chloro-bromo-chloride, the cis pairs in each case being optically active as enantiomorph pairs. These six isomers are shown in Diagram VII, page 109.

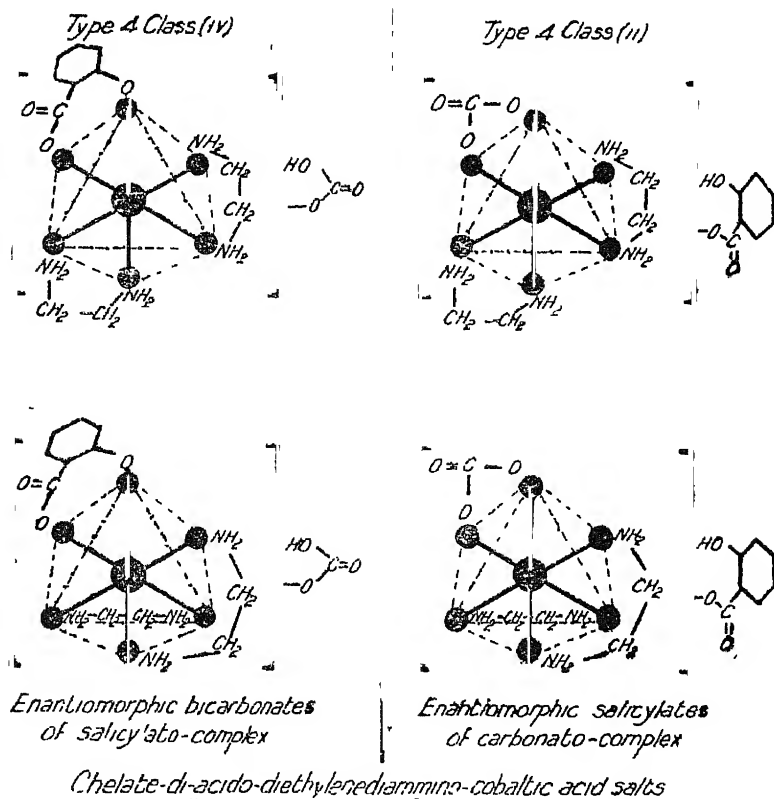
Representatives of type 4 are incapable of exhibiting ionisation isomerism due to univalent ions, but may exhibit ionisation isomerism due to bivalent ions if one of the chelate groups is bivalent. The two optically active isomers of salicylato-diethylenediammino-cobaltic bicarbonate of class 4 (iv), for example, are ionisation isomers of the two optically active isomers of carbonato-diethylenediammine

cobaltic salicylate of class 4 (ii). These four isomeric compounds are shown in Diagram VIII.

The whole of the foregoing cases of isomerism in compounds containing octahedral atoms relate to compounds

DIAGRAM VIII

*Ionisation Isomers*



containing only one octahedral co-ordination complex, but many cases have been discovered by Werner in which the isomerism is due to combinations between several octahedral co-ordination complexes, and a few cases were elucidated by him in which the observed isomerism is due to combinations of octahedral with tetrahedral complexes. Strictly

all metallic ammines are combinations containing tetrahedral complexes, for the nitrogen atom of each ammonia molecule is the focus of a tetrahedral co-ordination complex, which, however, owing to its symmetry, is not alone capable of giving rise to isomeric forms (see class I (ii) p. 97).

Similarly the nitrogen atoms of ethylenediamine are the foci of tetrahedral complexes, which, being of class I (iv), are also incapable of giving rise to isomeric forms. One of the carbon atoms of propylenediamine (tetrahedral class I (v) ),  $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$ , can give rise to optically



active isomeric forms, and octahedral complexes containing propylenediamine consequently give rise to at least two optically active isomers, even if the octahedral complex itself has no possibilities of isomerism. Werner was successful in obtaining, for example,<sup>1</sup> the whole of the ten optically active isomers of dinitro-propylenediammino-ethylenediammino-cobaltic salts, five from one isomer of propylenediamine and five from the other isomer. Reference to Tables 5 and 8 shows that the compounds belong to class 3 (v) and that four of the five isomers should be derived from the cis and one from the trans octahedral complex. The four cis and one trans optically active isomers were actually obtained with each form of propylenediamine, thus demonstrating conclusively not only the octahedral structure of the cobalt complex but the tetrahedral structure of only one carbon complex.

It is also of interest to observe that Werner at the same time obtained the complete set of partially and completely racemic compounds, i.e. racemic with respect to propylenediamine only, to cobalt only, and to both propylenediamine and cobalt. This series of optically active and racemic compounds must be considered one of the most outstanding of Werner's triumphs, and one of the most conclusive proofs for his co-ordination theory.

Most of the cases of combination between octahedral

<sup>1</sup> *Helv. Chim. Acta*, 1918, 1, 5

complexes relate to those containing two cobalt atoms, the so-called " $\mu$ -binuclear" complexes, in which one complex acts as a chelate group to the other by means of two atoms in the *cis* position. A typical example, due to Werner,<sup>1</sup> is imino-nitro-tetra-ethylenediammino-dicobaltic complex, which contains the imino and nitro groups in the *cis* position in each cobalt complex together with two ethylenediamine ("*en*") molecules,  $\left[ en_2 Co \begin{array}{c} \diagup NH_2 \\ \diagdown NO_2 \end{array} Co en_2 \right]$ . Each cobalt complex is separately of the general class 4 (iv) and should give rise to a pair of enantiomorphs, which are the same pair for either cobalt atom. As in the case of a bi-nuclear tetrahedral complex, only three combinations are possible of two uni-nuclear forms, the first combination consisting of two of the same enantiomorph, the second combination of two identical enantiomorphs of the other sort, and the third combination of an enantiomorph of each sort. The first two combinations are optical isomers whereas the third is optically inactive by internal compensation, i.e. a meso-form. These three isomers were all obtained, the inactive form being the first meso-compound to be obtained containing an "asymmetric" atom other than carbon. These three isomers are completely analogous to the three isomeric tartaric acids, and differ structurally only in containing two octahedral instead of two tetrahedral co-ordinating atoms.

In 1914, a long-known complex basic salt was shown by Werner<sup>2</sup> to contain four octahedral complexes, in which each of the three *cis* positions of a cobalt complex are common to one of three other cobalt complexes, the three last acting as three symmetrical chelate groups to a central atom, the quadrinuclear complex thus representing the two optically active forms of class 4 (i), both of which were obtained, the compounds being the enantiomorphous pair corresponding to the formula  $\left[ Co \begin{pmatrix} OH \\ OH \end{pmatrix} Co(NH_3)_4 \right]_3 Br_6$ .

<sup>1</sup> *Ber*, 1913, 48, 3674

<sup>2</sup> *Ibid*, 1914, 47, 3087.

The elucidation of the constitution of this complex salt threw a flood of light on the constitution of basic salts generally and of many complex minerals, particularly those of the apatite group, basic copper cadmibiomite, for example, having the structure,  $\left[ \text{Cd} \left( \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \right) \text{Cu} \right]_3 \text{B}_{12}$ , and apatite the structure  $\left[ \text{Ca} \left( \begin{smallmatrix} \text{O} \cdot \text{PO}_3 \\ \text{O} \quad \text{PO}_3 \end{smallmatrix} \right) \text{Ca}_3 \right]_3 \text{F}_2$ .

The phenomena to which Berzelius gave the name "isomerism" in 1832, but which had been noticed by Faraday in 1825, constitute the foundation for the whole theory of stereo-chemistry, and to its manifestations can ultimately be assigned the whole of the existing knowledge respecting the constitution of molecules and the chemical structure of atoms. Weiner's co-ordination theory is essentially a theory relying for its evidence on isomerism. Though Werner had shown in the early years of his theory that it was competent to explain the constitution and isomerism of hundreds of classes of chemical compounds, his theory was not very widely accepted until in 1911 he demonstrated the existence of optically active isomers, of cobalt co-ordination compounds.

This tardy recognition of the co-ordination theory has been due without doubt to the rather abnormal importance attached to optical activity by many of the leaders of modern chemical thought, who are specialists in the comparatively restricted field of organic chemistry. The carbon atom being of a tetrahedral nature is representative of a type to which only a few of the lightest elements conform, and Table 4, on page 97, shows that only four of the fourteen possible types of tetrahedral complexes can give rise to isomers, and that the whole of the isomers are *optically active*. Optically active compounds are therefore, necessarily, the outstanding feature of isomerism in organic chemistry. Even the optically inactive meso-isomers of organic chemistry are the result of two optically active foci in molecules, as has been shown on page 99 in connexion

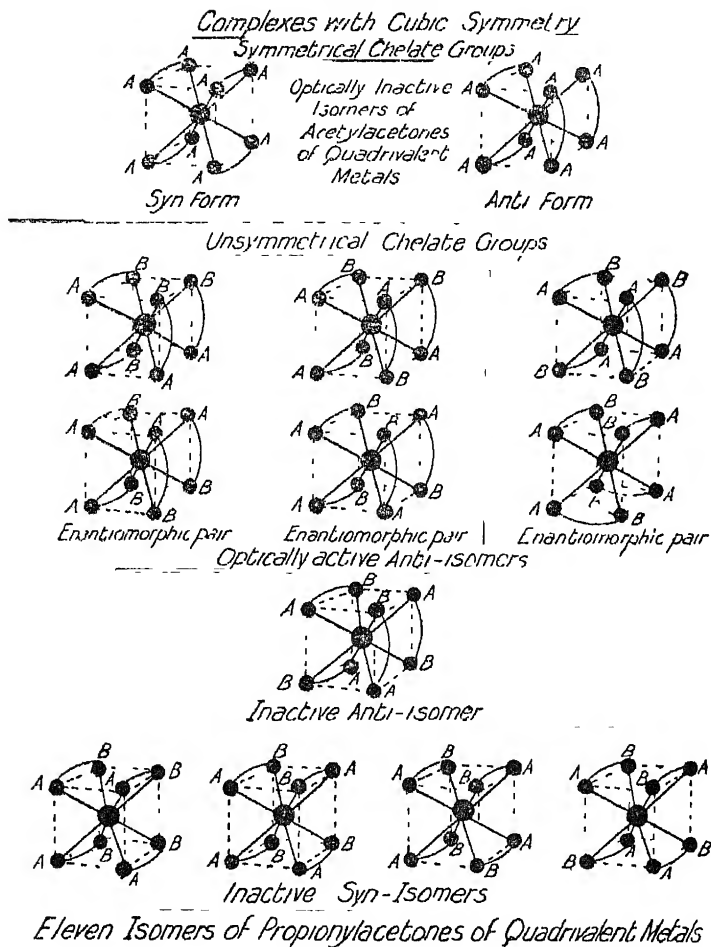
with meso-forms. The uninuclear stereo-chemistry of the organic domain is thus largely the stereo-chemistry of enantiomorphic co-ordination complexes. This is no longer true in the domain of inorganic chemistry, for a single octahedral co-ordination complex can give rise to isomers which are optically inactive, and their existence necessitates modification of the conception of the importance of optical activity in theories of isomerism. To the general failure to realise this fundamental difference between tetrahedral and octahedral isomerism, is to be attributed much of the common failure to appreciate the decisive nature of Werner's experimental evidence for his co-ordination theory.

Many complex compounds are known in inorganic chemistry to which it appears impossible to assign a co-ordination structure of six or less atoms or groups about a central atom, and it is usual to regard such compounds as complexes containing a nuclear atom with a higher co-ordination number than six. The commonest complexes are those to which the co-ordination number eight has been assigned to the central atom, for example, the zirconium, cerium, and thorium atoms in their tetra-acetylacetonates and related compounds. However attractive this analogical formulation may be it must be remarked that no case is known of the existence of isomeric forms of complexes to which the co-ordination number eight may be assigned.

Examination of the symmetry of the eight-point structure of the cube shows that it is capable of giving rise to five main types of complexes, non-chelate, mono-chelate, di-chelate, tri-chelate, and tetra-chelate, and that these five types include one hundred and nine classes, of which twenty-two are non-chelate, twenty-two mono-chelate, twenty-five di-chelate, twenty tri-chelate, and twenty tetra-chelate. The tetra-acetylacetonates should give rise to two optically inactive isomers, which may be described as *syn* and *anti* in orientation, while unsymmetrical diketones should give rise to eleven isomers, six anti enantio-

morphs, and one anti and four syn inactive forms (see Diagram IX) In no case have isomers been detected.

DIAGRAM IX



or near the atomic surface, and that six is the maximum number of subgroup elections that can appear near the surface of an atom or an atomic ion.

The evidence contributed by Werner's co-ordination theory to the theory of the structure of atoms may be summarised as follows. Atoms on combination gain or lose negative electric charges in accordance with their electro-negative or electropositive valency, the exterior of atoms is characterised by the possession of a definite number of symmetrically distributed points at which combination with other atoms occurs; these characteristic atomic superficial features are, in number, two for the hydrogen atom, four for the atoms from lithium to oxygen, four for most of the atoms of the periods of the periodic classification which include the halogen elements; commonly six for most of the atoms of the periods which include the "transition elements"; and four for most of the atoms in combination with oxygen as acids.

The interpretation of this evidence in terms of electrons will be given in later chapters on the electronic structure of atoms. It may be remarked that the evidence of the co-ordination theory is almost the only experimental evidence available at the present day for the determination of the number of electrons in the various sub-groups of atomic structure, just as the periodic classification is the sole experimental evidence for the determination of the number of electrons in the larger groups of atomic structure

## CHAPTER IX

### VALENCY AND SUB-ATOMIC CHEMISTRY

CAVENDISH had shown as early as 1767 that the equivalency between an acid and a base on neutralisation was not the equality of weight, and this fact is incorporated in Richter's law of equivalent proportions, applying to combinations between elementary substances as well as to compounds. The equivalent weight of a substance is the unit for the measurement of chemical operations. That the unit is a different weight for different substances is no hindrance in chemistry to the use of the unit, any more than the difference in weight of commodities is any hindrance to commercial operations equated in cash. Had the equivalent weights of substances ultimately been demonstrated to be identical with the weights of their ultimate particles, atoms or molecules, chemistry would have been a science of extreme simplicity, a science of the structure of molecules instead of, as it is and always has been, a science of the structure of atoms and the relation of the parts of atoms to the structure of molecules.

The facts that the equivalent weight of an atom is not always identical with the atomic weight, and that the various equivalent weights of an atom are integral multiples of the smallest equivalent weight, were summarised by Dalton in 1803 in his law of simple multiple proportions by weight. Though the precise values of atomic weights were not a matter of general agreement until after 1858, when Cannizzaro had securely established Avogadro's hypothesis, no doubt existed from the earliest days of Dalton's atomic theory that most atoms entered into chemical combinations in virtue of their possession of more than one equivalent weight. This combining capacity of an atom, called by Gerhardt in 1853 its "hydrogen atomicity," was identified, immediately after Cannizzaro's regularisation of atomic weights, as a characteristic of the atom no less definite and important than its weight, and,

under the name of valency, has been the foundation stone of the whole structure of modern chemistry.

Faraday's work on electrolysis in 1833-1834 disclosed that the equivalent weights of all elements are associated with the same quantity or charge of electricity, negative for some elements and positive for others, and led Clerk Maxwell in 1873 to infer that each molecule liberated in electrolysis parted with the natural unit of electric charge. Clerk Maxwell's suggestion was made more precise by Johnstone Stoney in the following year by the proposition of the natural unit of electrical charge as the quantity associated with the equivalent weight of an element or the rupture of one chemical bond. This unit, at first called the "electrine" but altered in 1891 to the now familiar "electron," is strictly an electrical unit derived from chemical considerations, and remained an electro-chemical hypothesis not admitted generally for twenty-three years, until its identification by Sir J. J. Thomson in 1897 as the negative electrical charge on a material unit about eighteen hundred times lighter than the hydrogen atom. Since that date the name electron has been definitely transferred from the negative electrical charge to the material particle carrying the negative charge.

In 1881, Helmholtz suggested the identification of units of chemical affinity, valency, with units of electrical charge or "atoms" of electricity, each chemical atom being assigned as many "atoms" of electricity as it possessed units of affinity or valency. Clausius had already, in 1857, suggested that molecules were to a small extent ionised in solution into parts carrying positive or negative charges, and it consequently followed from Helmholtz' suggestion that atomic ions in solution carried a number of positive or negative "atoms" of electricity in proportion to the valency existing in the combination.

In 1901, Neirst clarified Helmholtz' views by the suggestion that the laws of constant composition and of simple multiple proportions applied with equal force to

the quantities of electricity as to the quantities of matter taking part in a chemical reaction, and deduced from the fact that elements are electrically neutral in the free state, that the creation of charges on atoms in combination must arise by the exchange between atoms of positive for negative "atoms" of electricity or elections, common salt, NaCl, for example, being a compound in which the sodium and chlorine atoms on becoming ions have exchanged negative and positive electrons.

In 1902, Sir Oliver Lodge, in an address to the Institute of Electrical Engineers,<sup>1</sup> suggested that only negative electrons were transferred in chemical combinations, negative charges on atoms representing the acquirement of elections, and positive charges the loss of electrons, and his suggestion is the basis of all present theories of electronic reactions in chemistry. He further suggested that electrons in one atom could be utilised by another atom prior to their separation to form appropriately charged ions, and this may be regarded as the origin of the many subsequent theories of electron-sharing in non-ionised compounds.<sup>2</sup> Two years later<sup>3</sup> he suggested that, though the electric charges or electrons, to the transfer of which chemical combination between atoms is due, are indivisible, the forces resulting are not indivisible, and that, though the bulk of the lines of force might be utilised in binding the atoms together, some of the lines of force could be utilised in binding other molecules, thus giving rise to complex aggregates, and offering a feasible mechanism for the explanation of residual affinity. Some time later, P. F. Frankland<sup>4</sup> showed that Lodge's suggestions could be applied to the phenomena of ionic dissociation and catalysis, and to the combination of water of crystallisation and to molecular compounds generally.

<sup>1</sup> *J. Inst. Elect. Eng.*, 1902-3, 32, 45

<sup>2</sup> See also his *Modern Views on Matter*, Romnes Lecture, Oxford, 1903, and *Electrons*, 1906

<sup>3</sup> *Nature*, 1904, 70, 176.

<sup>4</sup> *Ibid.*, 1904, 70, 223

In 1908, Ramsay put forward the suggestion that electricity is one of the chemical elements, the atoms of which are the elections, on the grounds that the electrons are "atomic" in nature, have definite mass, exist free as molecules, and form compounds by combination with ordinary atoms, and crystallised Lodge's electron-sharing views in the statement that elections "serve as the bonds of union" between atom and atom.<sup>1</sup>

In the same year, Stark elaborated the conception of electron-sharing between atoms into a theory of chemical combination,<sup>2</sup> in which he regarded an electron *in* an atom as sending lines of force not only to its own positive part but also to the positive part of the chemically bound atom. This theory was considerably altered in 1915<sup>3</sup> in its application to organic compounds, Stark regarding the shared elections as in two atomic structures simultaneously, one such electron being equal to one chemical bond, except in the combination between carbon atoms and between carbon and hydrogen when two shared electrons were considered equivalent to one chemical bond.

In 1913, Bohm, in extending his dynamic theory of atomic structure to the combination between atoms,<sup>4</sup> suggested that the shared elections in a bond between atoms existed as a rotating ring of electrons perpendicular to the line joining the atoms, two electrons in the ring being equivalent to the bond between two hydrogen atoms or between a hydrogen atom and a carbon atom, and similar dynamic views were put forward by Kossel in 1916.<sup>5</sup> In Parson's magneton theory of atomic structure,<sup>6</sup> two electrons were regarded as forming one chemical bond between two like atoms, the two shared elections contributing to the formation of a group of two electrons in the atomic

<sup>1</sup> *J Chem Soc.*, 1908, 93, 778

<sup>2</sup> *Jahrb Radioaktiv Elektroniik*, 1908, 5, 125

<sup>3</sup> *Die Elektrizität im chemischen Atom*, Leipzig, 1915

<sup>4</sup> *Phil Mag.*, 1913, [6], 26, 857

<sup>5</sup> *Ann Phys.*, 1916, [4], 49, 229

<sup>6</sup> *Smithsonian Inst Publ.*, 1915, 65, No 11

structure of hydrogen and a group of eight electrons in the structure of other atoms.

In 1916, Lewis put forward a theory of valency based on static electrons otherwise almost identical with those of Parson and Kossel,<sup>1</sup> in which the outer or valency electrons of atoms were shared between two atoms so as to complete outer groups of eight electrons in each atom, two electrons being regarded as equivalent to one chemical bond.

The outstanding feature of nearly all these electron valency theories was the postulate of an outer completed group of eight electrons, after combination, in each atom, except hydrogen, the electron group in this case consisting of two electrons. The presumed necessity for this lay in the fact, recognised by Mendeléeff in 1871, that the maximum valency of any element is eight, illustrated by the tetroxides of ruthenium and osmium and the octafluoride of osmium. Reference to Mendeléeff's 1871 table (on page 71, Chap. VI) shows that this maximum valency of eight is exhibited only by elements which do not yield compounds with hydrogen, and that the highest valency of other elements is equal to the difference between eight and the valency towards hydrogen, or, in other words, that the sum of the electropositive and electronegative valencies of elements is equal to eight. This fact, recognised by Abegg and Bodländer in 1899<sup>2</sup> in their suggestion that the sum of normal and contra valency is eight, is of importance in theories of atomic structure, but it is not justifiable to conclude that the whole of the eight electrons discernible in valency combinations appear in the outer structure of any one atom, with the possible exception of osmium in the octafluoride. In this connexion it is significant that, with the solitary exception noted, all deductions, as to the presence of eight electrons in the outer parts of atoms, are made from compounds containing multivalent elements, particularly oxygen, and there is good reason to believe

<sup>1</sup> *Proc Nat Acad Sci*, 1916, 2, 586

<sup>2</sup> *Zeit anorg Chem*, 1899, 20, 453

that in most of such compounds each multivalent element acquires outright at least one of the electrons, thus halving the number of electrons. If it were universally true that two shared electrons are equivalent to each chemical bond, it would be necessary to assume that the eight chemical bonds in osmium octafluoride and tetroxide represented sixteen elections in the outer structure of osmium, an assumption definitely at variance with the eight-election postulate on which the two-electron bond claims to be founded. The same discrepancy obviously arises for every element having valency greater than four. It is permissible, therefore, to conclude, if the maximum number of electrons in the outer part of an atom be eight, that the chemical bonds of all elements having valency greater than four consist of not more than one electron per bond. If this must be conceded, it applies to nearly half of the known elements, and renders more than doubtful the general existence of two-electron bonds.

Examination of chemical compounds generally leads to the conviction that no simple rule exists for the determination of the number of electrons in a chemical bond, and that this number is a problem for experimental research on every bond in every chemical compound. The evidence gathered from compounds of valency greater than four appears to point to the existence of one shared electron per bond, and, as all these elements give rise to compounds more or less readily hydrolysable, it may be surmised that easily hydrolysable bonds contain only one electron whatever the valency of the atom concerned. The only elements that give rise to compounds unhydrolysable, or hydrolysable only with great difficulty, are the feebly electronegative non-metallic elements, such as carbon, nitrogen, phosphorus, and sulphur, and these together with oxygen, the element to which hydrolytic reactions are attributable, may be regarded as the elements in which two shared elections may be expected to exist in a chemical bond.

Theories based on the postulate of two electrons per chemical bond have multiplied to an extraordinary extent since 1916, and it is almost impossible to give an account of the various uses to which the hypothesis has been put by numerous writers and workers in the fields of both organic and inorganic chemistry as well as in physics. The most outstanding of the theories based on the two-electron junction is that of Langmuir,<sup>1</sup> and is merely, so far as valency is concerned, an amplification of Lewis's views. This theory postulates that the two-electron bond or "*co-valency*" is the invariable bond of chemical unit valency, and that the outer surface of every atom in combination, except hydrogen, consists of an invariable "*octet*" of electrons arranged with cubic symmetry. As has already been indicated this type of theory, based on two-electron junctions per bond and eight electrons per atomic group, completely fails in application to the whole of the elements having valency greater than four, and moreover to the whole of the elements which Werner has proved to be associated with six co-ordinated groups or atoms. This restricts the application of Langmuir's theory almost exclusively to hydrogen and the seven elements from lithium to fluorine, and, though the theory is claimed to be applicable to elements generally, it is noteworthy that nearly all the examples cited in the theory are compounds of carbon, nitrogen, and oxygen. It may further be remarked that no theory founded on a bond of two electrons can explain the existence of tri-atomic hydrogen, the ions of tri- and di-atomic hydrogen, the boron hydrides, nitric oxide, carbon compounds with triple bonds, and the non-existence of the tetra-, penta-, and hexa-fluoroethanes, compounds of six of the eight elements to which Langmuir's theory must be expected to be in complete accord. In addition to its bearing on valency, Langmuir's theory presents an interpretation of the periodic classification based on a scheme of atomic structure.

<sup>1</sup> *J Amer Chem Soc.*, 1919, **41**, 868, 1543; 1920, **42**, 274.

This portion of his theory will be dealt with in Chapter XIII.

Lewis has recently extended his theory of 1916, on which Langmuir's theory is founded, and, while retaining the covalency postulate of the two-electron bond, has rejected Langmuir's theory in so far as it postulates static electrons and an invariable atomic outer structure of eight electrons.<sup>1</sup> Lewis, however, has been no more successful than Langmuir in his explanation of many of the compounds to which Langmuir's theory is inapplicable, and his new theory necessitates so great elasticity in the outer groups of atomic structure that one is driven to conclude that this elasticity is necessitated not by experimental facts, but solely by his hypothesis of the invariable two-electron bond, and represents the last resource of a dying theory. The carbon compounds alone are so numerous and so varied in types and properties that it is inconceivable that any adequate explanation of them could be furnished by a theory involving merely pairs of equivalent electrons in the carbon bonds with other atoms. A sufficient body of evidence has now accumulated to indicate that the reactive electrons in carbon atoms in combination consist of at least two and probably three different types, and that minute changes in the structure of compounds suffice to convert electrons of one type into electrons of another type. It appears certain that theories of chemical valency must begin at a lower level than the surface of an atom, that the solution of the problem of valency must follow not precede the solution of the more general problem of atomic structure, and that, therefore, the problem of the number of electrons in any chemical bond will be the last solved of the problems of chemistry.

<sup>1</sup> *Valence and the Structure of Atoms and Molecules*, New York, 1923

## CHAPTER X

### RADIOACTIVITY AND SUB-ATOMIC CHEMISTRY

IN 1896, in the course of a search for substances spontaneously emitting Röntgen or X-rays, Becquerel discovered that the fluorescent double sulphate of uranium and potassium was capable of affecting a photographic plate even in complete darkness,<sup>1</sup> and later proved that this property was independent of the uranium salt used and of its previous exposure to daylight, thus demonstrating that the radiation produced was an intrinsic property of the element uranium. Two years later, Schmidt proved that the element thorium had radiative properties similar to those of uranium.<sup>2</sup>

Becquerel's further discovery in 1896 that uranium radiation had the property of discharging electrified bodies, that is, of making the surrounding air a conductor, rendered possible the accurate measurement of the intensity of even extremely feeble radiation, and his gold-leaf electroscope method is still in common use for the determination of radioactivity. The ease and rapidity of this method of measurement of radioactivity led Madame Marie Curie to the examination of a large number of minerals,<sup>3</sup> and, in conjunction with her husband, Pierre Curie, to the discovery of polonium, an intensely radioactive substance having properties allied to those of the element tellurium.<sup>4</sup> In the same year, they discovered the now well-known element radium,<sup>5</sup> which was proved to have properties very similar to those of barium. It is, however, probable that radium is more closely allied to strontium (both give intensely red flame colorations), just as thorium is most closely allied to zirconium, and uranium most closely allied to molybdenum. It is, in fact, a general observation that alternate members of a valency group in the periodic table show the greatest chemical resemblance, for example,

<sup>1</sup> *Compt. rend.*, 1896, **122**, 420.

<sup>2</sup> *Ibid.*, 1898, **127**, 1264.

<sup>3</sup> *Doctorial Thesis*, *Faculté des Sciences*, Paris, 1898.

<sup>4</sup> *Compt. rend.*, 1898, **126**, 175.

<sup>5</sup> *Ibid.*, 1898, **127**, 1215.

iodine and chlorine; bromine and fluorine, bismuth, arsenic and nitrogen; and antimony and phosphorus. The properties of the elements of the last period appear to indicate that this period resembles the 2nd long period rather than the 3rd, and it is probable, if the whole of the elements conceivable existed, that there would be eighteen members in the last period as in the 2nd long period, rather than about thirty members as in the 3rd long period.

The atomic weight of radium was found by Madame Curie in 1903, by the analysis of radium chloride to be approximately 225, and in 1907 she obtained the more accurate value, 226.2, by the analysis of a relatively large quantity (0.4 gram) of pure radium bromide.<sup>1</sup> The most recent determinations by other workers indicate that the figure, 226.0, represents the atomic weight of radium with great accuracy. Radium is the only element of the thirty-nine radioactive elements other than uranium and thorium, for which the atomic weight has been experimentally determined. It was isolated in the free state in 1910 by Madame Curie and Debierne, and found to resemble metallic barium. The free metal was found to have precisely the same radioactivity as the same weight of the metal in the form of its salts, thus demonstrating conclusively that radioactivity is an intrinsic property of an atom and independent of the operation of valency.

In 1899, Debierne discovered a new radioactive substance, actinium, allied in properties to the trivalent rare-earth elements. He was unable to separate it from admixed lanthanum owing to the minuteness of the quantity obtainable.<sup>2</sup> In the same year the Curies<sup>3</sup> showed that radium had the property of communicating radioactivity to bodies in its vicinity, and Rutherford independently showed that thorium had the same property.<sup>4</sup> In 1904, Debierne showed that actinium resembled radium and thorium in

<sup>1</sup> *Compt. rend.*, 1907, **145**, 422.

<sup>2</sup> *Ibid.*, 1899, **129**, 593, 1900, **130**, 206.

<sup>3</sup> *Ibid.*, 1899, **129**, 714.

<sup>4</sup> *Phil. Mag.*, 1900, [6], **49**, 1.

its capacity to make surrounding objects radioactive<sup>1</sup> Rutherford's experiments indicated that this property of thorium was due to the liberation of a gas or emanation (thoron) with radioactive properties, and Dorn in 1900 proved that radium liberated a similar emanation.<sup>2</sup>

In 1902, Rutherford and Soddy<sup>3</sup> came to the conclusion that the radium emanation had the properties of an inert gas of the same family as helium and argon, and suggested that the helium always found in radioactive minerals might be causally not casually connected therewith. Martin in the same year suggested that the radioactive elements were undergoing decomposition,<sup>4</sup> and Rutherford and Soddy<sup>5</sup> shortly afterwards put forward a hypothesis of radioactive disintegration and transformation, by which it was assumed that a definite proportion of the atoms of a radioactive element are unstable and disintegrate by the emission of one or more of the three known types of radiation associated with radioactive elements, the residues of the original disintegrated atoms being atoms of new elements, of which another but definite proportion are unstable and further disintegrate.

The three types of radiation from radioactive substances are  $\alpha$ -rays, consisting of heavy positively charged particles not materially deflected by a magnet;  $\beta$ -rays, consisting of very light negatively charged particles (electrons) easily deflected by a magnet; and  $\gamma$ -rays not affected by magnetic or electric fields and identical with X-rays, except in being usually more penetrative, thus being in fact ordinary light pulses of the shortest known wave-length.

In 1903, Ramsay and Soddy<sup>6</sup> proved conclusively that radium emanation disintegrates by the formation of the inert gas helium, and that therefore the  $\alpha$ -rays, detected by

<sup>1</sup> *Compt rend*, 1904, 138, 411

<sup>2</sup> *Abh. Naturforsch Ges Halle*, 1900

<sup>3</sup> *Phil Mag*, 1902, [6], 4, 580

<sup>4</sup> *Chem News*, 1902, 85, 205

<sup>5</sup> *Phil Mag*, 1902, [6], 5, 576

<sup>6</sup> *Proc Roy Soc*, 1903, 72, 204, 1904, 73, 346

Rutherford and Soddy<sup>1</sup> as the only radiation from the emanation, consisted of helium. This may be regarded as the first direct experimental proof that atomic disintegration and transformation are realities. In 1909, Rutherford and Royds proved by spectroscopic methods<sup>2</sup> that  $\alpha$ -rays in all cases consisted of positively charged helium atoms, thus demonstrating the reality of disintegration and transformation for the whole of the radioactive elements giving rise to  $\alpha$ -radiation.

With the exceptions of radium and helium it was not certain that any of the radio-products were in fact chemical elements, until Ramsay and his co-workers had determined the chief physical constants of radium emanation, the density of which was found by Whytlaw-Gray and Ramsay to be 111.5, it thus having the highest density and the highest molecular weight of any known gas.<sup>3</sup> It having been confirmed that radium emanation is completely destitute of chemical properties, i.e. valency, it was placed by analogy in the same periodic group as the inert gases. If, like them, it is a monatomic gas, its atomic weight must be double its density, indicating the atomic weight, 223, from Gray and Ramsay's density measurement, a value confirmed by Perkin's (1908) and Debierne's (1910) experiments on the rate of effusion of the gas. To mark his identification of radium emanation as a definite chemical element, Ramsay proposed for it the name, *niton*, though it is still often referred to as radium emanation or radon.

In 1905, Debierne<sup>4</sup> showed that actinium, like radium, yields helium in disintegrating to form actinium emanation or actinon, discovered by him in 1903. In the same year, Soddy and Mackenzie<sup>5</sup> proved that radium is produced by the disintegration of uranium. Two years later, Boltwood showed that this disintegration involves the production of

<sup>1</sup> *Phil. Mag.*, 1903, [6], 5, 445.

<sup>2</sup> *Ibid.*, [6], 17, 281

<sup>3</sup> *Proc. Roy. Soc.*, 1911, A, 84, 536

<sup>4</sup> *Compt. rend.*, 1905, 141, 383.

<sup>5</sup> *Phil. Mag.*, 1907, [6], 14, 272

an intermediate element to which he gave later the name ionium, he having at first assumed that this element was actinium.<sup>1</sup> Boltwood further showed that ionium was chemically inseparable from thorium, and differed from it only in possessing different radioactive properties. In 1907, McCoy and Ross<sup>2</sup> showed that thorium and radiothorium, one of its disintegration products, were chemically inseparable, and differed only in radioactive properties. Three years later Marckwald<sup>3</sup> showed that radium and mesothorium<sub>1</sub> were similarly chemically inseparable, yet differed in radioactive properties.

In 1911, Soddy<sup>4</sup> independently came to the same conclusion as Marckwald as to the non-identity but chemical inseparability of the two bodies radium and mesothorium<sub>1</sub>, and proposed the term **isotopes** for all elements chemically inseparable, i.e. having identical chemical properties and valency, but differing usually in atomic weight and always in radioactive properties. In 1913, Fleck<sup>5</sup> pointed out that all the then-known radioactive elements, over twenty in number, corresponded with only ten positions in the periodic classification, and that five of these positions were occupied by the five elements, thallium, lead, bismuth, thorium, and uranium, all of which were known before radioactivity was discovered. It was, consequently, evident that many of the radio-elements were not only isotopes of existing elements but of one another, and that the disintegration products of an element were often its isotopes.

Many suggestions had been made prior to 1913 as to the rule or law underlying radioactive disintegrations and transformations, for it had become abundantly evident that particular transformations were associated with specific types of radiations and were accompanied by expulsion of

<sup>1</sup> *Amer J Sci.*, 1907, [4], 23, 93, 1908, [4], 25, 365

<sup>2</sup> *J Amer Chem Soc*, 1907, 29, 1709

<sup>3</sup> *Ber*, 1910, 40, 3429

<sup>4</sup> *J Chem Soc*, 1911, 99, 72

<sup>5</sup> *Ibid* 1913 103, 381 and 1053

positive helium atoms or  $\alpha$ -particles, and negative or  $\beta$ -particles or electrons, and emission of  $\gamma$ -radiation or X-rays. A. S. Russell,<sup>1</sup> early in 1913, formulated a scheme for the particular case of the transformation of uranium to ionium, by which the valency decreased two on the loss of an  $\alpha$ -particle and increased one on the loss of a  $\beta$ -particle, uranium of valency 6 thus passing into uranium  $X_1$  of valency 4 by the loss of an  $\alpha$ -particle, this passing into uranium  $X_2$  of valency 5 by loss of a  $\beta$ -particle, then into uranium<sub>2</sub> of valency 6 by loss of a second  $\beta$ -particle, and then into ionium of valency 4 by loss of a second  $\alpha$ -particle. A similar scheme was put forward by Fajans.<sup>2</sup> In the same year Soddy formulated the complete law of radioactive change, known as the **Law of Radioactive Group Displacement**,<sup>3</sup> which states that an element, on expulsion of a doubly-charged helium atom or  $\alpha$ -particle, passes into an element two less in valency, and, on expulsion of a  $\beta$ -particle or negative electron, passes into an element one greater in valency.

Certain well-defined exceptions to the displacement law must be recognised. Bivalent radium emits both  $\alpha$ - and  $\beta$ -particles but passes into non-valent niton as if only an  $\alpha$ -particle had been emitted. Quadriivalent radioactinium similarly emits both sorts of particles, and  $\gamma$ -rays as well, but passes into bivalent actinium X as if only an  $\alpha$ -particle had been emitted. Quadriivalent radiothorium similarly emits both sorts of particles but passes into bivalent thorium X as if only an  $\alpha$ -particle had been emitted. Neither bivalent mesothorium<sub>1</sub> nor trivalent actinium emit  $\beta$ -particles in changing to trivalent mesothorium<sub>2</sub> and quadriivalent radioactinium respectively. At the points of branching of both the radium series and the actinium series, where both  $\alpha$ - and  $\beta$ -particles should be emitted, only one type of particle is emitted, quinquevalent radium C passing

<sup>1</sup> *Chem News*, 1913, 107, 49

<sup>2</sup> *Phys Zeit*, 1913, 14, 131 and 136, *Ber*, 1913, 48, 422

<sup>3</sup> *Chem News*, 1913, 107, 97, *Jahrb Radioaktivität*, 1913, 10, 188

into trivalent radium  $C_2$  without emitting  $\alpha$ -particles, and quinquevalent actinium C passing into sexavalent actinium  $C_1$  without emitting  $\beta$ -particles.

The substantial accuracy of the law of group displacement may, however, be accepted, as the foregoing discrepancies are largely negative in character and the appropriate radiation may yet be discovered. The positive exceptions consist in the emission of  $\beta$ -particles or electrons, and this emission has been attributed to the ionisation of the atoms by the loss of an outer electron due to some peculiarity in the method of  $\alpha$ -particle emission.

The law of radioactive group displacement involves that unit change in electric charge is accompanied by unit change in valency, the loss of the *doubly*-charged helium or  $\alpha$ -particle accompanying *decrease* of *two* in valency, and the loss of *one* negative electron or  $\beta$ -particle accompanying *increase* of *one* in valency. It is evident that atoms must consist of a large number of positive helium particles and negative electrons, for, in the change from uranium to lead, eight  $\alpha$ -particles and seven  $\beta$ -particles are lost in the fourteen valency transformations. It is equally evident that the electrons lost cannot be the valency electrons of uranium, which has six valency electrons, for, not only are seven electrons in all lost, but the transformations result four times in sexavalent elements with six valency electrons. In fact after thirteen of these transformations involving the loss of seven electrons, the resulting element, polonium, has six valency electrons, being sexavalent like uranium.

As the loss of a helium particle from an atom must be accompanied by the diminution of atomic weight by 4, the atomic weight of helium, and can be compensated chemically by loss of two  $\beta$ -particles, it is evident that atomic weight is not chemically characteristic of atoms. This is illustrated by the fact that quadrivalent thorium after the loss of an  $\alpha$ -particle changes to the element mesothorium<sub>1</sub> of atomic weight less by 4, which further loses two successive electrons, without change in atomic weight, changing

successively into trivalent mesothorium<sub>2</sub> and quadrivalent radiothorium, the last an element chemically indistinguishable from the original thorium. Not only may chemically identical elements have the same or different atomic weight (isotopes), but chemically different elements may thus have identical atomic weights, e.g. mesothorium<sub>1</sub>, mesothorium<sub>2</sub>, and radiothorium. Different elements with identical atomic weight are described as **isobars**, and numerous sets of triplet and doublet isobaric elements are known.

The following table includes all the known radioactive elements the mutual relationships of which have been determined, valency (in roman numerals) and atomic weight, known or assumed (in figures), being shown in brackets.

TABLE 10

Uranium Series	Actinium Series	Thorium Series
U (vi, 238.2)		Th (iv, 232.15)
$\alpha$		$\alpha$
UX <sub>1</sub> (iv, 234)	Pa (v, 230)	MsTh <sub>1</sub> (ii, 228)
$\beta$	$\alpha$	$\beta$
UX <sub>2</sub> (v, 234)	Ac (iii, 226)	M Th <sub>2</sub> (iii, 228)
$\beta$	$\beta$	$\beta$
U <sub>2</sub> (vi, 234)		
$\alpha$		
Io (iv, 230)	RdAc (iv, 226)	RdTh (iv, 228)
$\alpha$	$\alpha$	$\alpha$
Ra (ii, 226)	AcX (ii, 222)	ThX (ii, 224)
$\alpha$	$\alpha$	$\alpha$
Nt (0, 222)	An (0, 218)	Tn (0, 220)
$\alpha$	$\alpha$	$\alpha$
RaA (vi, 218)	AcA (vi, 214)	ThA (vi, 216)
$\alpha$	$\sigma$	$\alpha$
RaB (iv, 214)	AcB (iv, 210)	ThB (iv, 212)
$\beta$	$\beta$	$\beta$
RaC (v, 214)	AcC (v, 210)	ThC (v, 212)
$\beta$	$\beta$	$\beta$
RaC <sub>1</sub> (vi, 214)	AcC <sub>1</sub> (vi, 210)	ThC <sub>1</sub> (vi, 212)
$\alpha$	$\alpha$	$\alpha$
RaC <sub>2</sub> (iii, 210)	AcC <sub>2</sub> (iii, 206)	ThC <sub>2</sub> (iii, 208)
$\beta$	$\beta$	$\beta$
RaD (iv, 210)	AcD (iv, 206)	ThD (iv, 208)
$\beta$	(Actinium-lead)	(Thorium-lead)
RaE (v, 210)		
$\beta$		
Po (vi, 210)		
$\alpha$		
RaG (iv, 206)		
(Ra-lead)		

In addition to the foregoing thirty-nine elements, two other radioactive elements, uranium Y and Z, have been detected. Both emit  $\beta$ -rays, but in neither case are their immediate generators known, though both are derived from uranium. Uranium Y is usually regarded as immediately derived from either uranium or uranium<sub>2</sub> by an  $\alpha$ -ray emission, and as being the progenitor of protactinium by a  $\beta$ -ray emission, thus forming the link between the uranium and actinium series, the latter being a branch series of the former. The main objection to this assumption appears to be that either uranium or uranium<sub>2</sub> must emit two different sorts of  $\alpha$ -rays, and such should be distinguished by difference in range. The Geiger and Nuttall Law, however, indicates that the range of the  $\alpha$ -particles is a function of the "period of half-life" of the emitting element. As the "period of half-life" is a radioactive constant for each element, difference in range is evidence of the existence of different elements. It may be inferred, therefore, that neither uranium nor uranium<sub>2</sub> can be the immediate progenitor of either uranium Y or uranium Z.

All the three known cases of branching of a series are due to the emission of two different types of rays, the disintegration following either an  $\alpha$ -ray or  $\beta$ -ray emission. It would therefore appear by analogy that uranium X and uranium Y are not produced from an element giving rise to already known  $\alpha$ -ray emission. If, however, an element can disintegrate in two different ways, emitting in both cases similar rays of the same range, there appears to be no objection to either of these elements being the immediate product of uranium or uranium<sub>2</sub>.

One of the curious features of the three series of radioactive elements is that in all three the course of transformation is identical for seven successive transformations, and that these seven transformations include similar types of branching of each series at corresponding points. Ionium, radioactinium, and radiothorium, each after two  $\alpha$ -ray emissions yield an emanation which is an inert gas, niton,

actinon, and thoron respectively. Each of these, after two successive  $\alpha$ -ray and one  $\beta$ -ray emission yield an element, C, emitting both  $\alpha$  and  $\beta$  rays, so that two products are obtained,  $C_1$  and  $C_2$ , yielding by single different emissions the same product. Radium C thus yields both radium  $C_1$  and  $C_2$ , both of which pass to radium D; actinium C yields both actinium  $C_1$  and  $C_2$ , both of which pass to actinium D; and thorium C yields both thorium  $C_1$  and  $C_2$ , both of which pass to thorium D. These three series of seven transformations thus give isotopic elements at each stage, the final stage yielding the three D isotopes of lead. In the uranium series the disintegration passes through three more stages yielding another isotope of lead, radium G or radium-lead. It seems probable that the two D isotopic products of actinium and thorium are not end members of their series, but pass, by analogy with radium D, through three corresponding stages to form two elements also G isotopes of lead.

On page 132 it was indicated, in the fourteen transformations from sexavalent uranium to quadrivalent radium G (radium-lead), that seven electrons are expelled as  $\beta$ -rays. This, however, cannot represent the whole of the electrons lost, because the valency changes are not taken into account. In an  $\alpha$ -ray change the valency diminishes by two, and two electrons must be expelled from the valency group of the atom. In a  $\beta$ -ray change the valency increases by one, and one electron must be gained by the valency group of the atom. If the expelled electron leaves the neutral atom completely, an electron must be captured by the valency group of the now positively charged atom to neutralise it and increase its valency by one. If the expelled electron does not leave the atom, it must remain in the valency group of the neutral atom as a valency electron. In either event the  $\beta$ -ray change does not result in an atomic net loss or gain of electrons. It consequently follows, in the eight  $\alpha$ -ray and seven  $\beta$ -ray changes from uranium to uranium-lead, that eight sets of two or sixteen electrons

must be lost completely in the radioactive processes. As lead is quadrivalent and thus possesses at least four valency electrons, it is evident that the original uranium atom must have contained sixteen plus four or twenty electrons, and as the element has a valency of six, it follows that the radioactive processes disclose in uranium fourteen electrons other than those in the valency group.

Further, since the radioactive changes from uranium to niton result in the reduction of the valency from six to zero, and as the removal of two electrons from niton results in radium A with six valency electrons, it must be inferred that niton has a group structure of eight electrons which is readily degraded to a group of valency electrons, varying from six for the isotopes of polonium to three for the isotope of thallium. It may likewise be inferred that the niton group of eight electrons is present in the isotopes of the elements uranium, protactinium, thorium, actinium, and radium, in addition to a group of electrons characterizing their valency. Not only must an eight electron group be present in all the isotopes of these five elements, but the absolute identity in the properties of the three inert gases, niton, actinon, and thoron, definitely shows that the arrangement of these eight electrons is identical in these three gases, and also, therefore, in the isotopic elements from which they are derived by successive removals of valency electrons.

The foregoing atomic structures for the thirty-nine radioactive elements have been deduced solely from experimental evidence, and are independent of any theory or hypothesis whatever as to atomic structure, and it must be regarded as certain that the whole of these elements have atomic structures of similar type, i.e. that the structures of the atoms of smaller atomic weight represent stages in the structural arrangements of the atoms of higher atomic weight, even when the higher atomic weight atoms are not those that yield the lower by disintegration.

In view of the remarkable similarity in the properties of

the elements, radioactive and non-radioactive, isotopic and non-isotopic, of the same periodic group, as chemical ions or free atoms it may be inferred that the whole of the known elements consist of atoms constituted on the uniform plan to which the radioactive elements conform. This plan in the case of radioactive elements has been shown to consist of groups of eight electrons in the inert gases and the elements of atomic weight up to uranium, and of the same group, though incomplete, in the case of radioactive elements of atomic weight less than the radioactive inert gases. By analogy the atoms of the non-radioactive inert gases also contain a group of eight electrons, and the same applies to the elements immediately following each inert gas. This is borne out by the fact that the elements preceding and following each inert gas have valency increasing by one unit from two to six in all cases, and from one to seven in one case. This includes more than half the known elements. The elements to which the analogy cannot be applied are those series in which more than seven elements occur without an intervening inert gas. These are the elements of the middle of the Mendeléeffian long periods of the periodic table, known as the transition groups or series. Except that these elements must contain the eight-electron groups of inert gases of lower atomic weight, the electronic structures of these elements cannot be determined by reference to the structures of the radioactive atoms, as these do not include a sufficient number of members of a transition series.

As the element helium is not preceded by a group of multivalent elements, it is not permissible to assume, on the radio-element analogy, that it contains a group of eight electrons. The facts that hydrogen with only univalency is the only element preceding helium, and that helium is capable of yielding the doubly-charged  $\alpha$ -particle by loss of two electrons, involve that helium, unlike all the other inert gases, possesses a group of only two electrons, and that successive electrons are added in subsequent

elements until the next inert gas is reached after the addition of eight electrons. The structures of the known inert gases can therefore be determined, at least in part, helium consisting of one group of 2 electrons; neon of two groups, 2 and 8; argon of three groups, 2, 8, and 8; krypton of four groups, 2, 8, 8, and 8; xenon of five groups, 2, 8, 8, 8, and 8; and niton of six groups, 2, 8, 8, 8, 8, and 8.

The law of radioactive group displacement indicates that every unit increase in valency is accompanied by unit loss of negative electric charge, or, in other words, that in passing from one element to the element next higher in periodic group number, the number of valency electrons increases by one while the total number of electrons in the atom is actually unchanged. Extending the law for valency increases to non-radioactive elements, involves that in passing from one valency group to the next higher, the total number of electrons is increased by one, for no electron is lost by  $\beta$ -ray emission, while the valency electrons increase by one. It therefore follows that every increase in the number of the periodic group of an element is accompanied by an equal increase in number of electrons.

In passing from argon to krypton, eighteen successive unit increases in number of the periodic group occur, and consequently krypton must contain 18 more electrons than argon. As argon has already been shown to have 8 of these in one group (the inert gas group completed in passing from univalent copper via septavalent bromine) the group of eighteen electrons can be dissected into a group of 10 and a group of 8, krypton thus consisting of 2, 8, 8, 10, and 8 electrons or 36 in all.

A similar argument applies to xenon, which, taking account of the unknown eka-manganese, must consist of 2, 8, 8, 10, 8, 10, and 8 electrons, or 54 in all.

From xenon to niton, 29 elements are known, and 2 others are missing from the periodic group 7, making 31 possible valency changes, involving the addition of 31 electrons, 8 of which are accounted for in the final inert gas group, niton

thus having the structure 2, 8, 8, 10, 8, 10, 8, 23, 8, or 85 electrons in all, and uranium a similar structure with the addition of 6 valency electrons, making 91 electrons.

As atoms are neutral structures, a positive charge must exist for every electron in the structure of an atom. Further as the weight of electrons is negligible in comparison with the weight of atoms, each electron being about 1845 times lighter than the atom of the lightest atom hydrogen, the whole of the mass of atoms must be located in their positive charges, two of which are known to exist in the radioactive product, the  $\alpha$ -particle. It has been indicated that the helium atom contains at least two outer electrons, removable to form the  $\sigma$ -particle, and it is certain that hydrogen consists of one easily removable electron and one positive charge or nucleus responsible for its entire atomic weight. It is inferable that the helium positive particle is the nucleus of a system of two outer electrons, and that every element is built up of a positive nucleus or nuclei and an independent system of electrons.

The general law suggested by radioactivity transformations has already been indicated, that the atomic structures of all elements follow the same constitutional plan. This law applied to helium indicates that it must follow the plan of hydrogen in which the electron is accompanied by a single positive nucleus, helium thus consisting of four electrons and four positive particles, to account for its atomic weight of 4. It has already been shown that the evidence points to a single group of two electrons in helium removable to form the  $\alpha$ -particle of radioactive changes. The remaining two non-removable electrons of neutral helium must therefore be firmly associated with the four positive charges. This complex of four positive particles and two negative electrons carrying a net positive charge of two can be identified definitely with the  $\alpha$ -particle, thus being describable as the helium nucleus. Lithium with univalency and atomic weight 7 must be derived from helium by the addition of three positive particles and three

negative particles or electrons. The law of atomic plan indicates that the helium outer group of two electrons must persist in lithium, which being univalent must therefore consist of three outer electrons. The remaining four electrons must be associated with the seven positive particles as a nucleus, which is derived from that of helium by the addition of three positive particles and two electrons. Similarly beryllium (atomic weight 9) consists of 2 valency electrons, and a helium-group of two electrons, associated with a nucleus of 9 positive particles and 5 electrons. Neon (atomic weight 20) consists of an inert-gas group of 8 electrons, and a helium-group of 2 electrons, associated with a nucleus of 20 positive particles and 10 electrons, and xenon (atomic weight 130) consists of successive groups from the surface inwards of 8, 10, 8, 10, 8, 8, 2, or 54 outer electrons, associated with 130 positive and 76 electrons forming a nucleus.

In general if the atomic weight of an element be  $W$  and the number of outer electrons be  $N$ , the number of positive particles in the nucleus is equal to  $W$ , the number of nuclear electrons is equal to  $W - N$ , and the net positive charge on the nucleus is equal to  $N$ .

The foregoing considerations do not enable any precise position in the atom to be allocated to the nucleus, nor do they indicate that the nucleus may not consist of subsidiary nuclei scattered about the surface or interior of an atom. The fact that the emission of helium nuclei from radioactive elements is not accompanied by free or attached electrons appears to indicate that the helium nuclei are either extraordinarily minute as compared with electrons and thus do not collide with electrons, or that the helium nuclei are located on the atomic surface. The latter suggestion is negatived by the fact that isolated helium nuclei on or near the surface of an atom would be in close juxtaposition with many of the electrons of the valency and outer electron groups, and would thus readily acquire electrons and form neutral helium atoms, the atom thus

rapidly completely disintegrating by the loss of neutral helium atoms. Radioactive changes, however, invariably produce doubly-positively charged helium nuclei, and the disintegration process comes to a definite end in all cases with the formation of lead, an element of very high atomic weight.

The only conclusion to be drawn is that the helium nuclei are not located on or near the surface of any atom, and that the helium nuclei are extraordinarily small even compared with the electron. The simplest structure, conforming with the whole of the evidence from radioactive and non-radioactive elements, is that of a very small central positive nucleus, containing the whole mass of the atom, surrounded by successive groups of electrons, the order of the groups being that indicated already for niton and uranium on pages 138 and 139.

The system of atomic structure above outlined is based entirely on the interpretation of experimental facts by means of a suggested law of uniform atomic plan inferred from radioactivity phenomena, and is independent of theories of atomic structure based on the dynamics of electrically charged particles. It will be shown in later chapters that the latter lead to an essentially similar system of atomic structure, and that a combination of the two systems results in atomic structures capable of offering a harmonious explanation of most of the known chemical and physical phenomena attributed to atoms

## CHAPTER XI

### ATOMIC PHYSICS

THE existence of two opposite kinds of electrification had been recognised as long ago as the early part of the eighteenth century, and Franklin in 1750 put forward the "one-fluid" theory in which all non-electrified matter was assumed to possess a normal amount of the single electric fluid, positive electrification being an excess and negative electrification a deficiency of the electric fluid. Franklin further assumed that the electric fluid was material and consisted of extremely small particles, capable of moving without resistance through ordinary matter. Except that his electric particles were positive particles, Franklin may be said to have anticipated in a remarkable fashion the modern conception of the negatively charged material electron. Franklin's one-fluid hypothesis was however shown to be incapable of explaining a large number of electrical phenomena without further equally far-reaching assumptions, and it was abandoned in favour of the two-fluid hypothesis, in which electricity was assumed to be of two opposite types, positive and negative, and was not regarded as necessarily granular in structure or even material in nature.

About a century later, Weber<sup>1</sup> expanded Franklin's hypothesis of electric particles into a theory of the structure of matter, which incorporated the two-fluid theory of electricity. Weber postulated two contrasting types of electric particles, positive particles devoid of weight and negative particles responsible for the whole of the weight of matter. An atom was represented as a number of positive particles revolving round a massive central negative particle. Except for the interchange of electrical signs, this theory very closely resembles the modern theory of the atom containing rotating negative electrons and a massive central positive nucleus. Weber further regarded an electric current as a flow of weightless positive particles

<sup>1</sup> See Ch. IV, p. 50.

through the matter of an electric circuit, and applied the theory to an explanation of a great number of electrical and magnetic phenomena, and postulated the variation in mass of electric particles in virtue of their velocity.

Weber's theory of electric particles with mass varying with velocity was rejected by contemporary physicists, though Clerk Maxwell admitted in 1873 that Faraday's laws of electrolysis could be explained only on the ground of a constant irreducible unit of electric quantity. In developing his "Electromagnetic Theory of Light," however, Clerk Maxwell definitely rejected the conception of discontinuous electrical quantities, and made use of the conception of electrical quantities susceptible of infinitesimal variation. This theory of the continuous nature of energy and electrical changes was greatly developed by Kelvin, Heaviside, and Sir J. J. Thomson, and became known as the "classical theory," and postulated the existence of a continuous ether in and by which the radiations of heat, light, and electricity were propagated. The classical theory of electricity and energy chiefly concerned matter in bulk, but was largely divorced from matter and applied most successfully to the radiation of energy in free space. In recent years it has proved to require very considerable amendment in its application to the particles of matter, in which radiation of all kinds has its ultimate origin. Had Clerk Maxwell accepted rather than rejected Weber's theory of electric particles, it is more than possible that the discontinuous character of the energy changes resulting in radiation would have been elucidated long prior to the establishment of Planck's "quantum theory" of 1900.

Clerk Maxwell's deduction in 1873 of the unit or atom of electricity in electrolysis, was followed in 1874 by Johnstone Stoney's postulate of the natural unit of electric charge, the electrone (now electron), and by his identification of it in the rupture of each chemical bond. In 1881 Helmholtz suggested the identity of electricity and chemical

affinity, unit affinity or valency being measureable by the number of units of electrical charge passing in electrolysis, and in the same year Sir J. J. Thomson showed that an electric charge must possess inertia or mass in virtue of its velocity, and calculated the rate of variation of such mass with velocity.<sup>1</sup>

In 1880, Crookes, as the result of his investigations of the nature of the cathode rays formed on the passage of electricity at high voltages through rarefied gases, came to the conclusion that these rays were material and carried negative electric charges, yet did not consist of solid, liquid, or gaseous particles, and suggested that they constituted a fourth form of matter, for which he proposed the term "radiant matter."<sup>2</sup> The material nature of these cathode rays, their power of penetration of matter, and their similarity whatever the gas operated with and whatever the material of which the cathode was made, suggested that the material particles of which the rays are composed are a constituent of all matter, and in 1891, Johnstone Stoney applied to these particles the name electron, and regarded their charge as identical with the fundamental unit charge proposed by him in 1874.<sup>3</sup> He further attempted to show how, in the classical theory of light radiation, electrons vibrating within an atom could give rise to the light radiation causing the bright lines in spectra.

In 1895, Lorentz<sup>4</sup> showed that many optical and electrical phenomena were susceptible of explanation on the assumption that oscillating or vibrating negatively charged particles existed in matter, and predicted several spectral phenomena which were later experimentally confirmed.

Two years later Sir J. J. Thomson announced that the cathode rays consisted of corpuscles, each having mass very

<sup>1</sup> *Phil. Mag*, 1881, [5], 11, 229

<sup>2</sup> *Proc Roy Soc*, 1880, 30, 469

<sup>3</sup> *Scient Proc Roy. Dublin Soc*, 1891, 583

<sup>4</sup> *An Attempt at a Theory of Electrical and Optical Phenomena in Moving Bodies*, Leiden, 1895.

much less than that of the hydrogen atom, and carrying a negative electrical charge of the same order as the electron predicted by Johnstone Stoney in 1874.<sup>1</sup> In the same year Kaufmann<sup>2</sup> and Wiechert<sup>3</sup> obtained similar results, and the mass of the electron is to-day known with an accuracy little less than that of the atom, and is about 1845 times less than that of the hydrogen atom.

In 1900, Planck<sup>4</sup> put forward the hypothesis that radiation is emitted or absorbed by oscillating or vibrating electric particles in a discontinuous manner, such that energy lost or gained by a vibrating particle is proportional to the frequency of vibration of the particle. He further assumed that the energy emitted or absorbed by the vibrating particle could not be emitted or absorbed in a continuously varying manner, but only in integral multiples of a minimum quantity, a "quantum" of energy, and that the proportionality between energy and frequency was converted into equality by multiplying by a constant. This constant, known as "Planck's Constant of Action," was assumed to be the same for all vibrating particles in every sort of matter. A vibrating particle having a frequency of vibration  $\nu$  could therefore emit or absorb energy only in amounts of  $h\nu$ ,  $h$  being Planck's constant. This theory originally applied to the explanation of heat-radiation, and extended from oscillating to rotating electric particles, forms the basis of Bohr's theory of atomic structure and the explanation of optical and X-ray spectra elaborated by Bohr, Sommerfeld, and others.

In 1903, Lenard<sup>5</sup> came to the conclusion that the electrons of the cathode rays, led out of a cathode tube through a thin metallic "window," were absorbed by the air only after traversing such distances as indicated that only an extremely small proportion of the space in atoms is impen-

<sup>1</sup> *Phil Mag*, 1897, [5], 44, 293

<sup>2</sup> *Wied Ann*, 1897, 62, 589

<sup>3</sup> *Wied Ann Supp*, 1897, 21, 443

<sup>4</sup> *Ann Phys*, 1901, [4], 4, 553

<sup>5</sup> *Ibid*, 1903, [4], 12, 714

triable by electrons. He assumed that the impenetrable parts of atoms, called "dynamids," consisted of one positive and one negative electron, and calculated that the impenetrable portions of an atom only amounted to a thousand-millionth of the volume of the atom, and regarded the number of dynamids per atom as proportional to the atomic weight.

In 1904, Sir J. J. Thomson, elaborating a suggestion of Kelvin, put forward a theory of atomic structure<sup>1</sup> in which an atom was assumed to consist of a sphere of positive electricity, having embedded in it a number of electrons or corpuscles equal to the positive charge, the electrons arranging themselves symmetrically in rings in accordance with the electrostatic forces.

Between 1906 and 1911, the investigations of Rutherford and of Geiger, and their co-workers, on the scattering of  $\alpha$ -particles from radioactive sources in passing through matter, led Rutherford in 1911 to propose the theory of the nuclear atom, known as the "Rutherford atom,"<sup>2</sup> in which the whole mass of the atom is regarded as concentrated on a minute positively charged central nucleus, surrounded by a number of negative electrons equal in total charge to the charge on the nucleus. Subsequent investigations have amply confirmed the reality of this type of structural atom, which forms the basis of all existing theories, dynamic and static, of atomic structure.

The work of Geiger having indicated that the charge or the atomic nucleus is approximately one-half of the atomic weight, van den Broek<sup>3</sup> put forward the hypothesis that the charge on the atomic nucleus is equal to the number of the element in the sequence of elements arranged according to atomic weights, or the nuclear charge is equal to the "atomic number."

In 1913, Bohr, then working with Rutherford in Man

<sup>1</sup> *Phil Mag*, 1904, [6], 7, 237, 8, 548, 1905, [6], 10, 695, 1906, [6], 11, 769

<sup>2</sup> *Ibid*, 1911, [6], 21, 669

<sup>3</sup> *Nature*, 1911, 87, 78, 1913, 92, 373 and 476, *Phys Zeit*, 1911, 12, 490  
1913, 14, 32

chestei, put forward<sup>1</sup> a theory of the structure of the hydrogen and ionised helium atoms which incorporated Rutherford's theory of 1911 (the small nuclear atom with surrounding electrons), van den Broek's hypothesis of the same year (the equality of the nuclear charge, the number of atomic electrons, and the atomic number), Planck's quantum theory of 1900 (the discontinuous nature of the energy radiated by a vibrating electric particle in an atom), and Balmer's law of the hydrogen optical spectrum of 1885<sup>2</sup> as generalised by Rydberg in 1890<sup>3</sup> and Ritz in 1908.<sup>4</sup> Bohr assumed that an atomic electron, circulating round the nucleus in virtue of the attractive force between the opposite electrostatic charges on nucleus and electron, could travel in circular orbits at fixed distances from the nucleus, proportional to the squares of successive natural numbers, without the expenditure of energy in radiation. In the classical theory of electro-dynamics based on Newton's and Kepler's laws of motion, an electric charge could revolve round an attracting charge only in continually decreasing orbits until finally the charges coalesced, the energy of the circularly "falling" particle being continuously dissipated by radiation out of the system as electromagnetic light waves. The assumption of fixed orbits in Bohr's theory was, therefore, equivalent to the identification of uniform circular motion (in the classical theory involving centripetal acceleration) with rectilinear uniform or non-accelerated motion. These fixed orbits, in which electrons circulate without emission or addition of radiant energy, were called by Bohr "stationary states," but are strictly states of motion of the electrons—they are only stationary states in the sense that the orbits in which motion takes place are fixed. Bohr further assumed that the difference in the energies of an electron in *any two* of the stationary states or fixed orbits represented twice the

<sup>1</sup> *Phil Mag*, 1913, [6], 26, 1 and 476.

<sup>2</sup> *Ann Phys*, 1885, [3], 25, 80

<sup>3</sup> *Compt rend*, 1890, 110, 394

<sup>4</sup> *Collected Works*, Swiss Physical Society, Paris, 1911

energy radiated or absorbed by the electron in being transferred from one orbit to another, and that the energy difference between *two consecutive* orbits was equal to twice the product of the frequency of the emitted radiation and Planck's universal constant. Numbering the orbits from the centre outwards from 1 onwards, the difference between any two orbit numbers represented the number of multiples of the unit or quantum of "*moment of momentum*" (not of *energy*) peculiar to each atom, and these numbers were accordingly called **quantum numbers** of the electron orbits in an atom. Combining Balmer's law, Kepler's and Newton's laws, and Planck's quantum relation, Bohr deduced that the lines of the hydrogen spectrum were given by the formula,

$$\frac{c}{\lambda} = \nu = \frac{2\pi^2 e^4 m}{h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right),$$

in which  $\lambda$  and  $\nu$  are the wave-length and frequency respectively of the emitted radiation,  $e$  the electron charge,  $m$  the electron mass,  $c$  the velocity of light,  $h$  Planck's constant, and  $n_1$  and  $n_2$  the quantum numbers of the final and initial orbits of the electron. He also showed that the lines of the similar spectrum of ionised helium (i.e. with one electron) were given by the same formula when the calculated frequencies were multiplied by four, the square of the charge, 2, on the helium nucleus.

In the same year, Moseley<sup>1</sup> began an investigation of the characteristic X-rays emitted by elements bombarded by cathode rays with the object of deciding whether the atomic weight or the atomic number of an element was the determining factor in the frequency of the X-radiation of elements, and for this purpose analysed the emitted X-rays into a spectrum for photography by a diffraction grating consisting of the regularly arranged atoms in a crystal, X-rays being of too short wave-length to be analysed by ordinary ruled diffraction gratings.

Two groups of spectral lines, known as the K and L

<sup>1</sup> *Phil. Mag.*, 1913, [6], 26, 1024, 1914, [6], 27, 703.

series, were examined by Moseley. In Bohr's theory the K lines are assumed to be due to the "falling" movement of an electron to the innermost orbit with the quantum number 1 from outer orbits, and the L lines to the "falling" movement of an electron to the second innermost orbit with quantum number 2 from outer orbits, these "falling" movements of an electron being consequent upon the ejection of an electron of quantum number 1 or 2, respectively, from the atom by the bombarding X-rays.

The simplified Bohr formula connecting the frequency of the radiation with the atomic number is,

$$\frac{c}{\lambda} = \nu = cN^2R \left( \frac{1}{1^2} - \frac{1}{2^2} \right), \text{ or } N = \sqrt{\frac{4}{3R\lambda\nu}} = \sqrt{\frac{4}{3R\lambda}},$$

where  $N$  is the nuclear charge,  $R$  is Rydberg's spectroscopic constant,  $c$  is the velocity of light and  $\lambda$  and  $\nu$  are the wavelength and frequency respectively of the emitted radiation, this formula applying for an electron moving from a 2 quanta to a 1 quantum orbit. Moseley, however, found in the case of the principal or  $\alpha$ -line of the K series of the elements examined that the equation was true only if  $N$  were reduced by approximately one unit, and that such amended equation gave a straight-line graph, thus proving that the atomic number of an element not the atomic weight is the characteristic factor in determining the electric charge on the atomic nucleus.

Moseley also showed that straight-line graphs are given on plotting frequencies of the L radiation against atomic numbers, though Bohr's simple equation was satisfied only by reducing  $N$  in the equation by a constant, approximately 7.4, for the L  $\alpha$ -line.

A calculation of the values of these two constants from the most recent determinations of the X-ray spectra of the elements indicates that "Moseley's constants" are anything but constant, and in the case of the K  $\alpha$ -line, the "constant" varies from about plus 0.8 to minus 2.3, and fluctuates in a highly irregular manner from element to

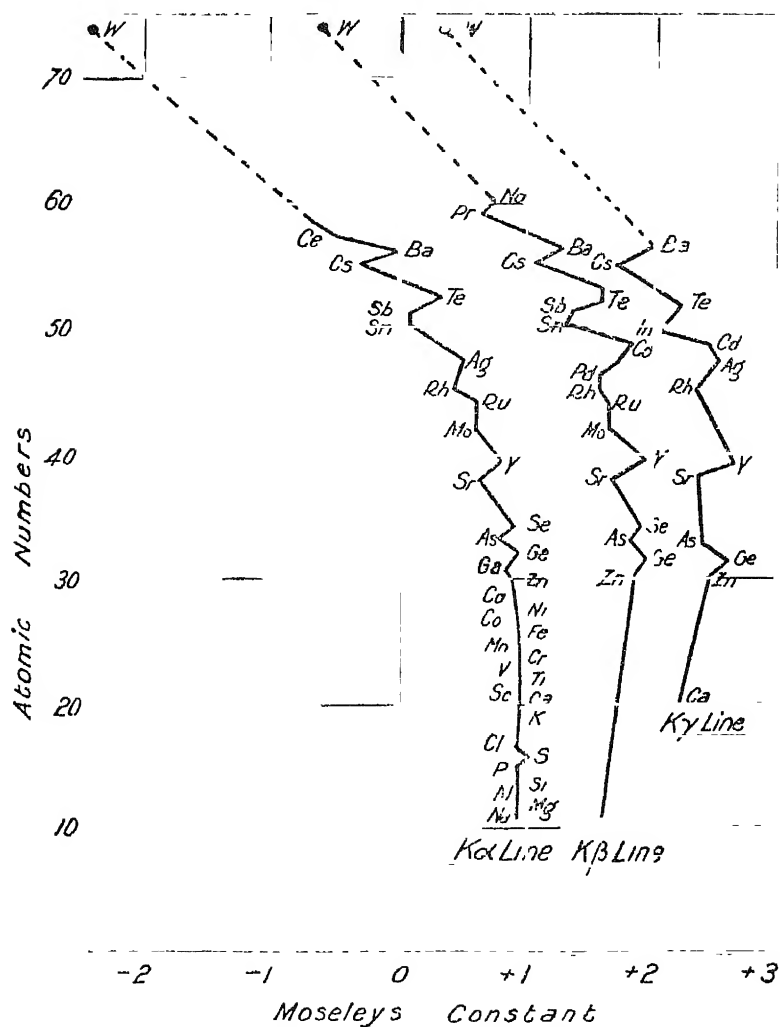
element. It approximates to 1 for elements only between atomic numbers 11 and 35, mostly examined by Moseley, and is practically zero for the elements of atomic number 49, 50, 51, 56, and 57, i.e. indium, tin, antimony, barium, and lanthanum. The values for "Moseley's constant" for the bulk of the elements for the  $\alpha$ ,  $\beta$ , and  $\gamma$  lines of the K series are shown in Diagram X. The value of the "constant" for the lines of the L series varies from nearly plus 14 to minus 4, but only from 6.8 to 7.4 for the L  $\alpha$ -line.

The discrepancy between the theoretical and calculated value of the nuclear charge disclosed by Moseley's work is presumed to be due to the screening effect of non-radiating electrons in the neighbourhood of the nucleus, the screening effect varying with the orbits of both non-radiating and radiating electrons. The peculiarity of the irregular values of the "screening-constant," in passing from element to element, and the close correspondence in the irregularities in the various lines of the K series do not appear to have been observed or to be susceptible of explanation in the foregoing way.

Though Moseley's method cannot suffice to determine the precise value of the nuclear charge, it indicates quite definitely that the nuclear charge increases by one unit in passing from element to element in the classification of the elements according to atomic weight and chemical properties, and consequently enables a decision to be made as to the precise order of the elements in the chemical classification in the cases of the three pairs of elements argon-potassium, cobalt-nickel, and tellurium-iodine, in which the atomic weights necessitate the order potassium-argon, nickel-cobalt, and iodine-tellurium, as against the foregoing indicated by their chemical properties. Moseley's values for the nuclear charges show clearly that the order is that of the chemical properties, i.e. that of the periodic classification. The nuclear charge, further, enables a decision to be made as to the number of missing elements in the periodic classification, and indicates that elements of the

## DIAGRAM X.

Moseley's  $K$  series Constant  
X-ray Spectra



atomic numbers 43, 61, 75, 84, 85, 86, 87, 89, and 91, are alone missing. Numbers 84, 86, 89, and 91, have been identified with the radioactive substances, polonium, niton, actinium, and protactinium, and their isotopes, but none of these, however, has been the subject of an atomic weight determination, and only one, niton, has been definitely characterised as a chemical element. The fact that the atomic number 61 alone is missing between lanthanum, 57, and lutecium, 71, indicates conclusively that the "rare-earth" transition period (see Ch. VI, p. 79) consists of 15 possible elements, and that, therefore, the 3rd long period of the periodic classification consists of 32 possible elements (see Ch. X, p. 138).

In 1886, Crookes<sup>1</sup> suggested that atomic weights might be averages of whole number atomic weights, elements thus being mixtures of atoms identical except in atomic weight. This suggestion was confirmed by the discovery more than twenty years later of isotopes among the radioactive elements, Soddy<sup>2</sup> in 1911 reviving Crookes' suggestion that elements generally were mixtures of chemically non-separable atoms in a constant proportion. In 1912, A. S. Russell and Rossi<sup>3</sup> showed that isotopes were not only identical in chemical properties but were identical even in optical spectra, such atoms consequently differing only in mass and radioactivity.

It may here be remarked, if the atomic weights assigned to the actinium series are correct, that isotopes may exist with identical atomic weights as well as identical chemical properties, e.g. radium C<sub>1</sub> and actinium A, both with atomic weight 214, radium D and actinium B, radium E and actinium C, polonium and actinium C<sub>1</sub>, all six with atomic weight 210. Such pairs of elements differ in no respect except radioactivity, their atoms being identical in mass, nuclear charge, number of electrons, valency, and

<sup>1</sup> *Brit Assoc Rep*, 1886, 558

<sup>2</sup> *J Chem Soc*, 1911, 99, 72

<sup>3</sup> *Proc Roy Soc*, 1912, A, 87, 478

general physical and chemical properties. The extent of this identity throws extreme doubt on the accuracy of the atomic weights assigned to the members of the actinium series, not one of which has had its atomic weight determined experimentally, nor even been definitely characterised as a chemical element. In order that no isotopes should have identical atomic weight it would be necessary to reduce the actinium series by six units in atomic weight.

In 1911, Sir J. J. Thomson<sup>1</sup> showed that the positive rays obtained in cathode tubes were material particles of atomic and molecular dimensions, and determined the absolute values of the masses of the atoms of many elements. The method of generating the positive rays was similar to that employed by their discoverer Goldstein in 1886,<sup>2</sup> positively charged atoms and molecules, created by ionisation-loss of electrons in front of the negatively charged cathode, being allowed to "fall" through a hole or channel pierced in the cathode. These "canal rays" were analysed into homogeneous rays of similar type by means of superimposed electric and magnetic fields, Sir J. J. Thomson thus being enabled to obtain photographs of impinging particles in the form of parabolas on the plates, each parabola being due to particles having the same ratio of charge to mass. In an examination of neon, parabolas were detected corresponding to atomic weights 20 and 22, the presence of doubly-charged atoms of calcium (atomic weight 40) and molecules of carbon dioxide (molecular weight 44) being ruled out. The only explanation possible was that neon (atomic weight 20.2) was a mixture of atoms of atomic weight 20 and 22, the former preponderating, as was confirmed by the comparative faintness of the 22 parabola. This constituted the first detection of isotopic atoms among the non-radioactive elements.

The existence was also proved of triatomic hydrogen, and the ordinary atom of hydrogen was obtained with one

<sup>1</sup> *Phil Mag*, 1911, [6], 21, 225, 1912, [6], 24, 209

<sup>2</sup> *Phil Mag*, 1886, 39, 691

positive charge, but not more than one, thus confirming that the atom of neutral hydrogen possesses only one negative electron. The molecule of hydrogen was also detected with *one* positive charge, but *never two* positive charges, proving that chemical combination, if due to electrons, need be due to no more than *one electron for a chemical bond*. This was further confirmed by the fact that triatomic hydrogen was never detected with more than *one* electron missing (or one positive charge), i.e. with less than *two* present of the three electrons, for a molecule of three linked atoms must contain at least two chemical bonds. It was also proved that the inert gases are always positively charged, never negatively, thus indicating that they can lose but not gain electrons. In general it was found that the electronegative elements alone could give negatively unit-charged atoms, whereas all elements could give positively charged atoms, the acquirement of electrons thus being parallel with the chemical property of electronegativity, and the loss of electrons being the common property of all elements. The maximum number of electrons lost by any atom was proved to be eight, a significant fact taken in conjunction with the chemical fact that the maximum valency for any element is eight.

Sir J. J. Thomson's researches on positive ray analysis have yielded results of extreme chemical importance, altogether apart from the question of isotopic elements. His results may be regarded as an experimental demonstration that chemical combination, measured numerically in valency, is due to the reactions of electrons, valency being numerically identical with electrons in the case of ionisable compounds, that electronegativity is identical with gain of electrons and electropositivity with loss of electrons, that one electron may suffice for the chemical bond in the case of non-ionising compounds; that the structures of the atoms of the inert gases, in no circumstances, accommodate any more electrons, that the atoms of hydrogen and helium cannot yield structures containing more than two

electrons per atom ; that the maximum number of electrons that an atom can lose is eight ; and that the maximum number of electrons that an atom can gain is one.

Sir J. J. Thomson's method of positive-ray analysis was further improved by Aston in 1919<sup>1</sup> by an adjustment of successive electric and magnetic fields so that the particles having the same ratio of charge to mass are focussed on to the photographic plate as lines, which are the images of the slit through which the rays pass. This arrangement, known as the mass-spectrograph, disperses the various types of rays over a wide range while giving sharp definition to each type of ray, and it has been possible to measure the masses of the atoms or molecules forming the rays with an accuracy of 1 in 1000. The most important result obtained has been the proof that the majority of the elements are mixtures of isotopic atoms having atomic weights which are integral multiples of one-sixteenth of the atomic weight of oxygen, or, in other words, that atomic weights are whole numbers. The only outstanding exception is hydrogen, with an atomic weight of 1.008. This has been "explained" by the supposition that part of the mass of all other atoms has disappeared in the condensation of the atomic nucleus from electrons and hydrogen nuclei. If all mass is merely the inertia of an electric charge, two opposite electric charges in very close juxtaposition will partially obliterate one another, with resulting diminution in inertia due to electric charge, i.e. loss of mass. In the case of helium, the nucleus of which is supposed to be made up of four hydrogen nuclei, called protons, and two electrons, the loss of mass is the difference between  $4 \times 1.008$  and 4, that is 0.032, the difference between the atomic weight of four free atoms of hydrogen and the observed atomic weight of helium.

It may be remarked that this "explanation" of the deviation of hydrogen from the "whole number rule" has

<sup>1</sup> *Phil Mag*, 1919, [6], 38, 707, 1920, [6], 39, 611, 40, 628, 1921, [6], 42, 140 and 436, *Isotopes*, London, 1922

no evidence to support it, and that some evidence exists which throws doubt upon it. According to the most recent work of Ellis<sup>1</sup> on the  $\beta$ - and  $\gamma$ -rays of radioactive elements, the electrons in the nucleus exist in quantum orbits similar to those of the outer electrons. It must be supposed that the electrons in the intra-nuclear orbits possess much greater orbital velocity (owing to the extremely minute size of the nucleus as compared with the atom) than the extra-nuclear electrons. As the K electrons of uranium have a velocity (125,000 miles per second or 67 per cent of light speed) nearly sufficient to add perceptibly to the mass of the electrons, the velocity of the intra-nuclear electrons, even in the case of helium, must be sufficient to make an appreciable addition to the mass of these electrons. Helium should consequently have a greater mass than four atoms of hydrogen, which has no intra-nuclear electrons, a deduction which is not borne out in fact. This does not necessarily indicate the non-existence of intra-nuclear quantum orbits with electrons whose speed is not a negligible fraction of the velocity of light. It may merely indicate that the nuclei of all elements, hydrogen not excluded, contain a number, possibly a very large number of electrons, and that the mass of all nuclei is due partly or entirely to the mass of electrons as a consequence of their velocity. It may yet be necessary to assume that the positive charge of electricity is totally divorced from mass, and that mass is a function of negative electricity. It is remarkable that our present theories of mass and positive electricity are founded less on any positive knowledge of positive electricity than on the negations known of negative electricity.

A different method of generating positive rays, due to Gehicke and Reichenheim<sup>2</sup> has been elaborated by Dempster,<sup>3</sup> in which a metallic salt is electrically heated on a

<sup>1</sup> *Proc Camb Phil Soc*, 1922, 21, 121.

<sup>2</sup> *Verh Dent Phys Gesell*, 1906, 8, 559, 1907, 9, 76

<sup>3</sup> *Phys. Rev*, 1908, 11, 316, 1921, 18, 415, 1922, 20, 631

hollow platinum anode and simultaneously bombarded by electrons from a cathode, and the liberated positive particles accelerated by a small electric field and focussed by deflection round a semicircle by a magnetic field. The advantage of the method is that it can be used for non-volatile compounds, whereas the cathode "canal ray" method is applicable only to gases which can be ionised in the space in front of the cathode. The results obtained by both Dempster and Aston, using Dempster's method, have largely confirmed and supplemented the facts elucidated by Aston, using Sir J. J. Thomson's modified method, that the majority of the elements are mixtures of isotopes conforming generally to the "whole number rule" of atomic weights. In the case of selenium the atomic weight of one of the isotopes, 82, is identical with the atomic weight of one of the isotopes of krypton, and these non-radioactive elements therefore contain isobaric atoms, many cases of which are known among the radioactive elements.

The very great energy of the massive helium nuclei ( $\alpha$ -particles) ejected from the atoms of the radioactive atoms, due to the enormous velocities of the ejected  $\alpha$ -particles (about 12,000 miles per second for the  $\alpha$ -particles from radium C), led Ramsay in 1907 to bombard other elements with them in the hope of disintegrating their atoms. Though Ramsay announced several cases of disintegration and transformation, using this method, his results have not been confirmed. Nevertheless this method has within very recent years in the hands of Rutherford,<sup>1</sup> and Rutherford and Chadwick,<sup>2</sup> led to what appears to be a real disintegration of one or more of the lighter atoms. When such energetic bombardment of hydrogen atoms takes place, some of the hydrogen atoms are propelled forwards with a velocity that gives them a range of travel of about 28 cms. in air, the  $\alpha$ -particles themselves, being

<sup>1</sup> *Phil. Mag.*, 1919, [6], 37, 537, 1921, [6], 41, 307; *Proc. Roy. Soc.*, 1920, A, 97, 374, *Nature*, 1922, 109, 614

<sup>2</sup> *Phil. Mag.*, 1921, [6], 42, 809, 1922, [6], 44, 417

helium atoms four times as heavy, having a range in air of only a quarter, i.e. about 7 cms. When, however, the gas bombarded was nitrogen, particles identified as hydrogen atoms, having a range of 40 cms, were obtained, and, after ruling out the possibility of impurities, Rutherford assumed that the hydrogen particles arose from the disintegration of atoms of nitrogen. Hydrogen particles of range greater than 28 cms were also obtained on bombarding compounds containing atoms of boron, fluorine, sodium, aluminium and phosphorus, having the atomic numbers 5, 9, 11, 13, and 15. In all of these cases hydrogen particles having a range greater than 28 cms. were also found to be ejected in the backward direction by the bombardment, though in the case of nitrogen, of atomic number 7, the backward range was only 18 cms. No particles having a range exceeding 28 cms. were obtained from the bombardment of lithium, beryllium, carbon, oxygen, neon, magnesium, silicon, sulphur, chlorine, argon, and potassium, having the atomic numbers 3, 4, 6, 8, 10, 12, 14, 16, 17, 18, and 19. The general conclusions are that long range hydrogen particles are obtained only from elements of odd atomic number, but not from any elements of atomic number less than 5 or greater than 15. Rutherford regards the result as conclusive evidence that the atoms giving rise to the long range hydrogen particles actually contain hydrogen nuclei (protons) in their nuclei, and that a real disintegration has been obtained. He has also announced that nitrogen and oxygen yield particles of range 9 cms. having an atomic weight of 3 and a double positive charge, and has suggested that these atomic nuclei contain particles of atomic weight three, i.e. consisting of three protons and one electron.

It is possible, however, that the hydrogen particles of mass 1, and the short-range particles of mass 3 do not come from the atoms bombarded, but from the bombarding helium nuclei of mass 4, and that the results are due to the disruption of the helium nucleus into two parts of masses

1 and 3, each part with one electron, the particle of mass 1 having its electron "brushed" off in its long travel before producing the scintillation by which it is detected, and the particle of mass 3 falling to pieces after a short travel to give rise to two hydrogen nuclei and one hydrogen atom, or one hydrogen nucleus and one ionised hydrogen molecule, just as ionised triatomic hydrogen falls to pieces on further ionisation. The unsymmetrical disintegration of the helium nucleus may be attributed to the unsymmetrical structure of the bombarded atoms of odd atomic number. Atoms of even atomic number may, on the other hand, disrupt the helium nucleus symmetrically into two ionised molecules of hydrogen, which would have a short range owing to their mass and thus allow the disintegration to be overlooked. Rutherford's results are truly evidence of disintegration of elements, but perhaps only of the radioactively-produced  $\alpha$ -particle or helium nucleus. Until this possibility has been definitely excluded, judgment may properly be withheld as to the precise nature of the disintegration actually effected.

ether shell, during the process of entry and ejection of ether particles, is constant over the whole surface of the shell no matter what its radius may be, i.e. no matter how far the wave has travelled in space. This transverse-compression wave meeting an electron will subject the electron to the pressure of the shell, and it then becomes a question as to whether the wave will continue by movement of ether particles or will move the electron. If the electron be moved and its volume is equal to that of the ether particles being transferred from shell to shell, the compression in the shell from which the electron moves must disappear and the whole spherical wave throughout space suddenly cease to exist, even though the electron occupy only a very small area of the whole spherical shell. The electron thus acquires the energy of the light wave. If the electron were originally in motion its kinetic energy would be increased by the foregoing amount, and so long as the electron travelled in space where successive displacements did not alter in the state of compression of ether particles the electron would continue to move with this fixed amount of kinetic energy. This could occur in space far from the nuclei of atoms or on the surface of shells of ether particles about a nucleus where the extent of compression was uniform. An electron could therefore travel with undiminished energy in the spherical shell surrounding an atomic nucleus. This spherical shell contains all equivalent Bohr orbits. If the electron were originally moving in such a shell it could find a place for uniform circular motion (without loss of kinetic energy) in any other shell or Bohr orbit.

The foregoing mechanism provides only for the exchange of energy between electrons and light waves and for the circulation of electrons in fixed orbits without loss of energy, and makes no provision for the exact positions of the various possible Bohr orbits, nor for any relation between the energy radiated and the wave length of light radiated in transfers of electrons from one orbit to another,

nor for the "quantising" of the successive orbits in equal amounts of moment of momentum or angular momentum. It is merely a qualitative picture and has no claims to reality. A simple extension of the mechanism, however, provides for the reflection of light by electrons but not by nuclei, and for the known fact that all reflected light is plane polarised, and indicates that the plane of polarisation is that of the electron orbit.

Bohr's theory of quantised circular orbits was originally applied to atoms, hydrogen and ionised helium, containing only one electron outside the nucleus, and was successful in indicating the precise positions of the various lines in the optical spectra of the two elements. It also predicted the existence of spectral lines later discovered, and assigned the correct value to the dimensions of the atom, and the exact value of Rydberg's spectral constant. It must therefore be admitted as a valid qualitative and quantitative mechanism for Rutherford's atom, and it is the only existing theory of the atom which is in conformity with the known facts of atomic structure and spectrum analysis. It must consequently be accepted that the atom of the physicist and the chemist is a dynamic atom, and theories based on static electrons must give place to it, no matter how difficult the conception of the dynamic atom may be for the mechanism of chemical combination.

Bohr's theory of simple circular orbits was considerably expanded by Sommerfeld's theory that elliptic orbits as well as circular orbits must be possible for electrons circulating round a nucleus, as in the case of astronomical bodies.<sup>1</sup> Sommerfeld's postulate was that an electron moves in an ellipse at one focus of which the nucleus is situated, and he utilised a mathematical expression for elliptic orbits, developed by Wilson<sup>2</sup> and almost simultaneously by himself<sup>3</sup> in 1915, characterised by two

<sup>1</sup> *Atombau und Spektrallinien*, Munich, 1919, *Atomic Structure and Spectral Lines*, London, 1923

<sup>2</sup> *Phil Mag*, 1916, [6], 31, 161

<sup>3</sup> *Mün Ber*, 1915, 459, *Ann. Phys*, 1916, 50, 125.

quantum numbers, a radial and an azimuthal quantum number, elliptical motion being a problem of two degrees of freedom of the moving particle, the position of which is determined by the radial distance from the focus and by the angle (azimuthal angle) between the variable radius and the major axis of the ellipse. Sommerfeld extended this mathematical expression to the equation of Bohr's form of Balmer's law. He showed that the energy of the elliptic orbit was identical with that of the circular orbit, the energy of the elliptic orbit being a function of the sum of the azimuthal and radial quantum numbers, whereas that of the circular orbit is a function of the azimuthal quantum number only, the radial quantum number becoming zero owing to the constancy of the radius. He further showed that the number of possible types of orbits was numerically equal to the number of ways of obtaining the quantum sum of the radial and azimuthal quantum numbers, being *one* for circular orbits wholly made up of azimuthal quantum number, and *n-1* for elliptic orbits having both sorts of quantum number equal to *n* in sum. The elliptic orbits for the sum number 2 are one, two for the sum number 3, three for the sum number 4, and so on. The sum of the quantum numbers or total quantum number thus represents one, two, three, four, etc., types of orbits, including both circular and elliptic, when the total quantum number is 1, 2, 3, 4, etc., or in general the total quantum number *n* represents *n* types of orbit. Bohr's form of the Simple Balmer Law,

$$\nu = \frac{2\pi^2 me^4}{h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right),$$

thus became

$$\nu = \frac{2\pi^2 me^4}{h^3} \left\{ \frac{1}{(a_1 + r_1)^2} - \frac{1}{(a_2 + r_2)^2} \right\},$$

in which  $a_1$  and  $r_1$  are the azimuthal and radial quantum numbers of the final orbit, and  $a_2$  and  $r_2$  are the corresponding numbers for the initial orbit of the electron giving rise to the radiation.

Further the fact that the total quantum number 2 could represent two orbits and the quantum number 3 three orbits indicated that the Balmer series in which an electron moves from a 3 to a 2 quanta orbit, necessitated that an electron in each of the three 3 orbits could move to each of the two 2 orbits, each simple line of the Balmer series of spectral lines thus consisting of six lines in two sets of triplets all close together, *if the energies of the electron in each orbit were slightly different*. Sommerfeld calculated that the energy of the various orbits should not be quite identical for the same total quantum number, and that the more elliptic orbits should have slightly greater energy in proportion to their eccentricity, owing to the slight increase in mass of the electron in virtue of its greater velocity when moving near the nucleus (at the ellipse focus).

Sommerfeld's prediction of this "*fine structure*" of each of the Balmer lines has been realised by the magnification and separation of the lines by more accurate spectroscopic methods, and the calculated extent of the separation of the lines agrees precisely with the observed separation. This may be accepted as very conclusive evidence for the reality of Bohr's theory as amended by Sommerfeld and for the variation of the electron mass with velocity (see Appendix).

The Bohr-Sommerfeld theory has been extended from the optical spectra of hydrogen and ionised helium atoms to the X-ray spectra of elements in general, and with slight modifications has proved capable of adequately accounting for the manifold phenomena, both qualitative and quantitative, of the numerous known X-ray spectral lines, and all the known lines have now been precisely allocated to the movements of electrons from outer to inner orbits consequent on the ejection of inner electrons on X-ray bombardment. The related series of X-ray spectral absorption bands have similarly been precisely allocated to the ejection of electrons from inner to outer unoccupied orbits or to outside the atom. The interpretation of the absorption

spectra in terms of the theory has led to very exact knowledge of the various types of electron orbits, which have been found to be more numerous than the simple form of quantised elliptic orbits indicated. It is now known that the quantum number 2 represents not two but three types of orbit, only one of which is circular, that the quantum number 3 represents not three but five types of orbit, only one of which is circular, and that the quantum number 4 represents not four but seven types of orbit, only one of which is circular.

In the simple theory of elliptic orbits, any particular orbit is represented by the notation  $n_k$ , where  $n$  is the sum of the radial and azimuthal quantum numbers and  $k$  is the azimuthal quantum number, the single K quantum or K orbit being  $1_1$ , the two L quanta or L orbits, being  $2_1$  and  $2_2$ , the three M quanta or M orbits being  $3_1$ ,  $3_2$ , and  $3_3$ , and so on. The new orbits proved to exist by the absorption spectra are characterised by the notation, K series  $1_{1a}$ , L series  $2_{1b}$ ,  $2_{1a}$ ,  $2_{2a}$ , the M series  $3_{1b}$ ,  $3_{1a}$ ,  $3_{2a}$ ,  $3_{2b}$ ,  $3_{3b}$ , or by the still newer notation,  $1_{11}$ ,  $2_{11}$ ,  $2_{12}$ ,  $2_{22}$ ,  $3_{11}$ ,  $3_{12}$ ,  $3_{22}$ ,  $3_{23}$ ,  $3_{33}$ ,  $4_{11}$ ,  $4_{12}$ ,  $4_{22}$ ,  $4_{23}$ ,  $4_{33}$ ,  $4_{34}$ ,  $4_{44}$ , thus including the one K orbit, the three L orbits, the five M orbits, and the seven N orbits. A similar scheme of notation has been applied to the O and P orbits known to consist of five and three types,  $5_{11}$ ,  $5_{12}$ ,  $5_{22}$ ,  $5_{23}$ ,  $5_{33}$ , and  $6_{11}$ ,  $6_{12}$ , and  $6_{22}$ .

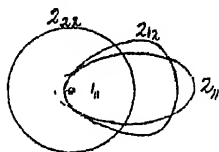
In circular orbits the *energy* of the circulating electron is *inversely* proportional to the *diameter*, and in elliptic orbits to the *major axis*, the diameter of circular orbits being identical with the major axis of elliptic orbits having the same total quantum number. The *diameters* of the circular and the *major axes* of the elliptic orbits are *directly* proportional to the *squares* of the *total quantum numbers*, while the *latera recta* (shortest chords through the nuclear focus) are *directly* proportional to the *squares* of the *azimuthal quantum numbers*. From the geometrical properties of the ellipse, it follows that the *minor axes* of elliptic orbits are

directly proportional to the product of the total and azimuthal quantum numbers, for the minor axis of an ellipse is equal to the square root of the product of the major axis and latus rectum. Similarly it follows that the distance between the foci of elliptic orbits is equal to  $n\sqrt{n^2 - k^2}$ , where  $n$  and  $k$  are the total and azimuthal quantum numbers. This expression reduces to zero for circular orbits, the foci being the single centre. For elliptic orbits the perihelion radius is equal to  $\frac{n}{2}(n - \sqrt{n^2 - k^2})$

this expression reducing to  $\frac{n^2}{2}$  for circular orbits, which is equal to the radius of the circle. From these expressions the forms of the various circular and elliptic orbits of any total and azimuthal quantum numbers can be readily constructed. All the possible types of orbit of total quantum numbers 1, 2, 3, and 4 are shown in Diagrams XI, XII, XIII, and XIV. For the simple circular and elliptic

### DIAGRAM XI

*Planar Representation  
of Electron Orbits*

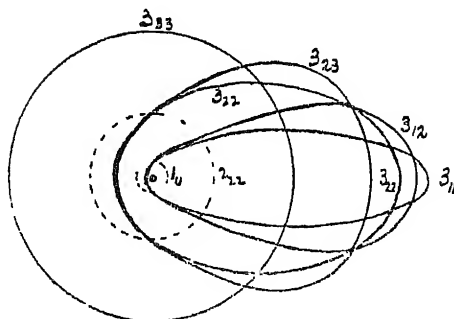


*Three Orbital Types of  
Quantum Number 2  
showing Unsymmetrical  $2_2$  Orbits*

orbits of the Bohr-Sommerfeld types, the orbits are  $1_{11}$ ,  $2_{11}$ ,  $2_{21}$ ,  $2_{22}$ ,  $3_{11}$ ,  $3_{22}$ ,  $3_{33}$ ,  $4_{11}$ ,  $4_{22}$ ,  $4_{33}$ ,  $4_{44}$ . The evidence of absorption spectra indicates one additional 2 quanta orbit,

## DIAGRAM XII

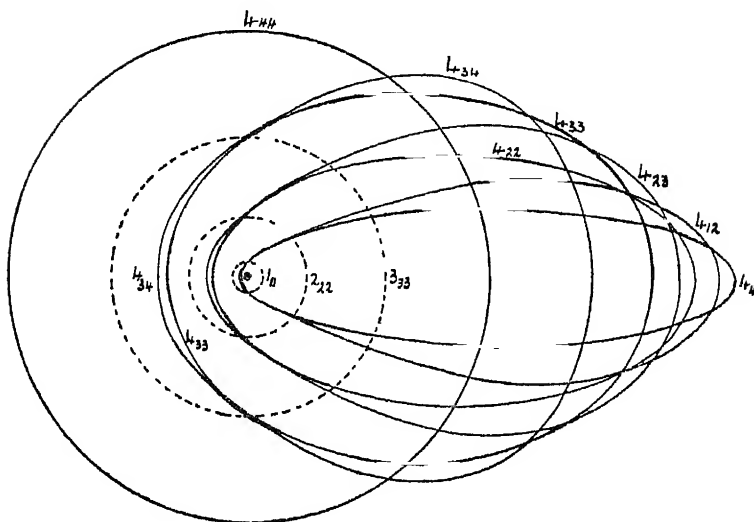
*Planar Representation of  
Electron Orbits*



*Five Orbital Types of Quantum Number 3  
showing Unsymmetrical  $3_{12}$  and  $3_{23}$  Orbits*

## DIAGRAM XIII

*Planar Representation of Electron Orbits*

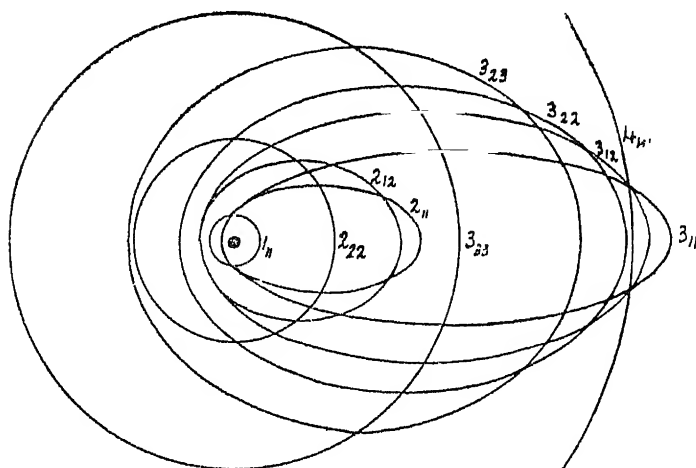


*Seven Orbital Types of Quantum Number 4  
showing Unsymmetrical  $4_{12}$ ,  $4_{23}$  and  $4_{34}$  Orbits*

two additional 3 quanta orbits, and three additional 4 quanta orbits. The Bohr-Sommerfeld theory has not, however, prescribed any forms for these additional orbits. From their azimuthal quantum numbers it may be inferred that they are closely related to the simple ellipses of a single azimuthal quantum number. Two possibilities are obvious, first that the orbits are unsymmetrical about the minor axis, and secondly that they are symmetrical about both

# DIAGRAM XIV

## *Planar Representation of Electron Orbits*



## *Alternative Configuration for Symmetrical $2_{12}$ $3_{12}$ and $3_{23}$ Orbits*

axes. The first type (see Diagrams XI, XII, and XIII) corresponds to an orbit of one azimuthal quantum near the nucleus and of the next higher azimuthal quantum number distant from the nucleus, the orbit thus having two different latera recta. The second type (see Diagram XIV) corresponds to an orbit having an azimuthal quantum number the mean of two consecutive azimuthal quantum numbers. It seems probable that the unsymmetrical type of orbit corresponds better to the evidence, and its formation may

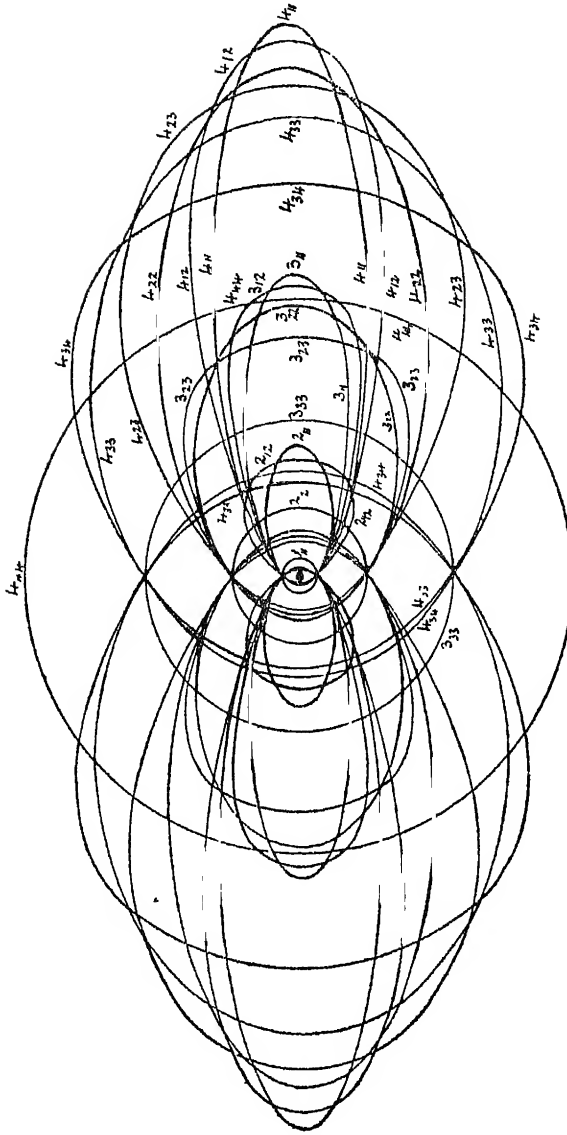
be attributed to the unsymmetrical type of electric field caused by an electron approaching the nucleus in an elliptic orbit. This corresponds with the known fact that orbits of two different azimuthal quantum numbers *are not* evident in the *optical* spectra of atoms having a single valency electron, and that such orbits *are* always evident in *X-ray* spectra, for in these cases atoms have pre-existing orbits of the simple elliptic type.

The unsymmetrical  $2_{12}$  orbit is shown in Diagram XI, the two unsymmetrical  $3_{12}$  and  $3_{23}$  orbits in Diagram XII, and the three unsymmetrical orbits  $4_{12}$ ,  $4_{23}$ , and  $4_{34}$  in Diagram XIII, and the whole of these are shown in Diagram XV, which indicates how the elliptic orbits penetrate not only into other elliptic and circular orbits, but even into the inner parts of similar orbits. These diagrams are no more than an indication of the complexity of interpenetrating orbits, and in a real atom the complexity is vastly increased owing partly to the many electrons in each class of orbit and to the fact that the orbits do not exist in a plane, but are symmetrically disposed about the nucleus in all the three dimensions of space. Only by an extreme licence in the use of words can each class of orbit be regarded as constituting an energy level or shell in an atom, for the orbital interpenetration makes a precise conception of levels impossible except in the case of truly circular orbits.

Sommerfeld's deduction that the energy of an electron circulating in an elliptic orbit is slightly greater than that of an electron in a corresponding circular orbit, due to the increase of electronic mass with increase in velocity, necessitated that the mass should increase as the electron approached the nucleus, and consequently that the electrostatic force of attraction should not be quite sufficient to retain the heavier electron in the path of the theoretical orbit, the electron thus travelling slightly *outside* the theoretical orbit. This continuous falling away of the electron in approaching the nucleus causes the real approaching path to lie further and further away from

DIAGRAM XV

*Planar Representation of Interpenetrating Electron Orbits*



*Orbits of 1, 2, 3 and 4 Quantum Numbers, in Duplicate,  
showing Orbital Interpenetration*

the theoretical orbit, and the electron to pass close to the nucleus at a perihelion position further round the nucleus in the same clockwise direction as the curved path of approach. On receding from the nucleus the velocity diminishes and the mass now decreases, the electron thus describing a path *inside* the theoretical orbit, and returning to an aphelion in a new position. As the circulation of the electron recurs, the actual path similarly diverges from the new theoretical path (see Appendix), the electron thus describing a path which is not closed and resembles an eccentric spiral. This type of path can be regarded as compounded of a circulation of the electron in a true ellipse the major axis of which is turning slowly about the focus, so that the perihelion of the ellipse moves in the direction of the outward portion of the ellipse and the aphelion in the direction of the inward portion of the ellipse.

This perihelion motion is commonly described as the relativity effect (see Appendix), and is analogous to the motion of the perihelion of the rapidly moving planet Mercury in describing its elliptic orbit about the sun. It is impossible to be content with ascribing this perihelion motion to a mathematical property of space, and it is natural to regard so-called relativity effects as due to a real material structure of space. The ether mechanism suggested at the beginning of this chapter provides a more or less adequate explanation of this perihelion motion. If the particles in the ether shells are increasingly compressed the nearer to the nucleus, an electron approaching the nucleus travels from a shell of less to a shell of slightly greater compression or density and is accordingly slightly retarded in its inward motion to the nucleus, and tends to travel in the circular path in a shell of uniform compression, i.e. in a true Bohr circular orbit. Put in another way, an approaching electron tends to be deflected so as to travel on an orbit of uniform moment of momentum, and the resultant path is a compromise between the initial and tending directions. This path is at every point a compromise between an

ellipse and a circle, and is thus a deformed ellipse the perihelion of which rotates in the same clock-wise direction as the electron circulates in the ellipse.

If the ether shells are of continuously decreasing density (the ether particles may be regarded as true spheres in free space and as deformed spheres approaching cubes when in compression) the further from an atomic nucleus, the ether round any collection of atoms, forming a mass of matter of any size, must decrease in density the further from the mass of matter, and perihelial motion of all planets in elliptical orbits should therefore occur, but will be observable only when the orbital velocity is sufficiently great to cause an appreciable increase in mass. A similar ether mechanism may be advanced to explain the bending of light rays, correctly predicted by the relativity theory, in passing close to the sun. The observed effect has been suggested by Sir Oliver Lodge as due to refraction of light waves possibly caused by the increased density of ether near large masses of matter.

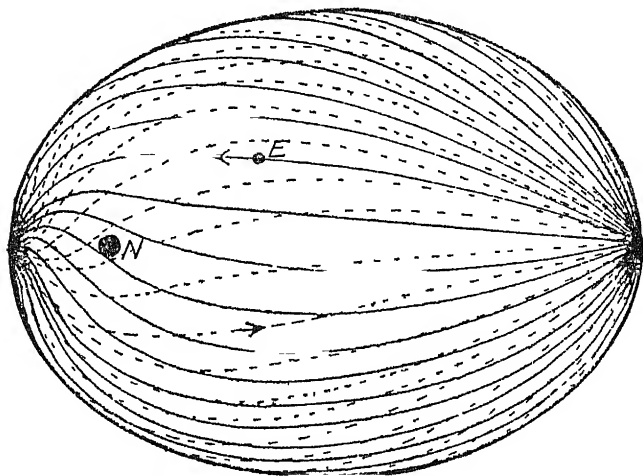
Sommeifeld's relativity effect for electrons in elliptic orbits was originally applied to atoms containing only one circulating electron. The effect must, however, exist to an enhanced extent in atoms containing many electrons in elliptic orbits, for the velocities of the electrons increase in proportion to the atomic numbers of the atoms. In the case of the one-electron atom the relativity theory predicts that the plane of rotation of the perihelion will be the plane of the orbit. This conception of orbital precession becomes impossible in the case of elliptical orbits where the number of electrons in such orbits are more than two or three, owing to the spatial distribution of the electron orbits. The conception of the planar motion of the orbital perihelion must therefore definitely be abandoned ; yet the increase of mass with increasing velocity must exist, for the separation of X-ray spectral lines clearly indicates that the electrons in the various orbits of the same total quantum number have not the same energies. This addition of

energy to the non-circular orbits must manifest itself in some form of orbit, though the numbers of the electrons and the extent of interpenetration make it impossible for the orbit to be an ellipse rotating in a plane containing the elliptic orbit. The positions of the various X-ray spectral lines with relation to one another, further, prove that the energies of the elliptical orbits are the same as if the ellipse were rotating in a plane, and it is thus evident that the ellipse is substantially preserved together with the extent of its precession. The extent of the precession effect may be regarded as a function of the diameter of the circle swept out by the rotating latus rectum, which is directly proportional to the square of the azimuthal quantum number of the elliptic orbit. In Sommerfeld's relativity effect this circle is described in the plane of the orbit. This may be ascribed simply to the absence of forces caused by other electrons. In the atom of many electrons, however, the mutual repulsions of the electrons with orbits spatially disposed about the nucleus will cause a precessing electron to remain within a small domain in space, though the attraction of the nucleus will maintain an effective elliptic orbit. This interaction of the nucleus and the surrounding electrons with a precessing electron will thus cause the precession effect to take place in a plane at right angles to the axis of the ellipse, thus fixing the perihelion in one place in space and consequently also the aphelion and the major axis. The resultant motion of the electron is the compounding of an elliptic motion with a circular motion at right angles, the path described by the electron being on the surface of the solid obtained by rotating the ellipse about its fixed major axis. The precession motion for elliptic orbits is thus confined to spiral paths described on the ellipsoid of revolution about the major axis, the electron twisting rapidly round a narrow spiral near the nucleus and a wider spiral near aphelion. A representation of this continuous spiral orbit of an electron having the quantum number  $4_3$  is shown in Diagram XVI.

This fixation of the major axis of elliptic orbits, while allowing for precession and increased energy with increased velocity, removes the chief obstacle to the utilisation of dynamic atoms in the chemical combinations between atoms for which the valency directions are definitely known in chemistry to be fixed in space round the atoms. This utilisation of dynamic atoms is obviously impossible so long as the aphelion of an elliptic orbit of a valency electron is

### DIAGRAM XVI

#### *Spatial Representation of Electron Orbital Domain*



*Precession Paths of a  $4s$  Electron moving on the Surface of an Imaginary Solid Ellipsoid of Revolution with Nucleus at the Focus*

regarded as necessarily rotating round the periphery of an atom.

The Bohr-Sommerfeld theory of atomic structure, being deduced from considerations of optical and X-ray spectra, specifies no more than the possible orbits in which electrons can rotate round an atomic nucleus, and in its present form can furnish no evidence as to the actual numbers of elec-

trons rotating in the various types of orbit. For the purpose of determining the total numbers of electrons in the orbits of any particular total quantum number, Bohr has had to enlist the aid of the chemical evidence, particularly that of valency and the periodic classification of elements according to atomic weight and chemical properties. This evidence, however, is of too general a nature to determine accurately the distribution of the electrons in the various subgroups corresponding to the various azimuthal quantum numbers of electrons with any particular total quantum number. This distribution can be ascertained only from the consideration of the minute details of the idiosyncrasies of the chemical properties of each element separately and in relation to other allied and contrasting elements, and this is peculiarly the knowledge of the chemist not the physicist. It may therefore be expected that future advances in the knowledge of the intimate structure of atoms will be made largely in chemistry, though it will be shown in Chapter XIV that the vast chemical knowledge already accumulated is now competent to decide the structural details for many of the elements.

## ATOMIC STRUCTURE AND THE PERIODIC CLASSIFICATION

RYDBERG'S<sup>1</sup> investigations of the numerical relations between the atomic weights of the elements in the periodic classification led him to conclude that the properties of the elements are periodic functions of a number, a common factor in atomic weights, and to propose a series of ordinal numbers for the elements, helium being number 4, by assuming two elements between hydrogen and helium. These ordinal numbers, reduced by 2, were identical with the present atomic numbers up to uranium, he thus being successful in determining the number of missing elements even before van den Broek had suggested or Moseley had established the precise values of the atomic numbers.

Rydberg was enabled to infer the number of missing elements by his discovery that the elements in the periodic classification fell into quadratic groups each consisting of  $4p^2$  elements,  $p$  being an integer increasing from 1 by unity for the various quadratic groups. The first group consisted of  $4 \times 1^2 = 4$  elements from hydrogen to helium, the second group (two periodic groups) of  $4 \times 2^2 = 16$  elements, the third group (also two periodic groups) of  $4 \times 3^2 = 36$  elements, and the fourth group of  $4 \times 4^2 = 64$  elements. Excluding the first group, the second and third periodic groups each thus consist of  $2 \times 2^2 = 8$  elements, the first two long periods each of  $2 \times 3^2 = 18$  elements, and the last period of  $2 \times 4^2 = 32$  elements. The various periodic groups in pairs were, consequently, equal to twice the squares of the natural numbers 1, 2, 3, and 4. These quadratic groups are now termed Rydberg's series and are expressed by the formula  $2(1^2, 2^2, 2^2, 3^2, 3^2, 4^2, \text{etc.})$ , or 2, 8, 8, 18, 18, 32, etc. After Moseley's determinations of the atomic numbers, Rydberg's series were seen to express accurately the number of elements in the successive periodic groups.

<sup>1</sup> *Zeit anorg Chem*, 1897, 14, 66, *Lunds Univ Arsskrift*, 1913, 9, 18

In 1919, Langmuir<sup>1</sup> adopted van den Broek's hypothesis as to atomic numbers and suggested that Rydberg's series expressed the number of elections in various successive shells about the nuclei of atoms, and on this basis elaborated a comprehensive theory of atomic structure. The hydrogen atom was assigned a structure of a nucleus and one election, helium a shell of two electrons, the elements from lithium to fluorine a partly completed additional shell of eight electrons, neon the completed additional shell of eight electrons, the elements from sodium to chlorine a partly completed further additional shell of eight electrons, argon the completed additional shell of eight, the elements from potassium to bromine an additional partly completed shell of eighteen electrons, completed in krypton, the elements from rubidium to iodine a further partly completed shell of eighteen electrons, completed in xenon, the elements from cæsium to bismuth a further partly completed shell of thirty-two electrons, completed in niton, and the elements from radium to uranium a further partly completed shell of thirty-two electrons.

Langmuir postulated that the radii of the shells were proportional to the natural numbers 1, 2, 3, and 4, and the areas of the shells to the squared natural numbers as in Rydberg's series. This involved the two outer shells of argon having the same radius and 16 elections, which were arranged in 8 pairs as a cubic structure with two electrons at each corner. The two outer shells of xenon similarly had the same radius and 36 elections in 18 pairs.

It was further postulated that the elections in incomplete shells were valency elections, by loss of or addition to which chemical combination occurred, with another atom, acquired elections completing a shell. As the maximum known valency is eight, Langmuir was driven to assume a natural tendency of atoms to form only shells of eight elections called octets. This further involved assigning to many atoms special forms of assumed inertness like the

<sup>1</sup> *J. Amer. Chem. Soc.*, 1919, **41**, 868 and 1543

inert gases, though no such inert forms are known. The chemically active element ion, for example, had to be assumed as inert in order to account for the bivalency of nickel, which was also assigned an inert form to account for the bivalency of zinc. If all valencies among elements had to be accounted for in a similar way it would be necessary to assume inert forms for more than half the known elements, and some very active elements, potassium for example, would require to possess inert forms corresponding to valencies of four or more different elements.

Langmuir adopted Lewis's postulate of 1916 that chemical combination between atoms, giving rise to non-ionising compounds, is due to the sharing of two electrons per chemical bond so that each atom completed a shell of eight electrons by the sharing process. It has been indicated in Chapter IX, that the postulate of two electrons per bond is not compatible with an octet structure for elements having valency greater than four nor for elements giving rise to compounds with a co-ordination number greater than four, and that this applies to all but a very few of the known elements. It was also indicated that the two-electron bond is incapable of explaining many types of compounds containing hydrogen, boron, carbon, nitrogen, oxygen, fluorine, and chlorine. It may further be remarked that the two-electron bond, called by Langmuir a covalency, is incapable of explaining the non-ionising and inert hexafluorides of sulphur, selenium, and tellurium, which contain on the covalency basis four more electrons than the next higher inert gases, and the same argument applies to many of the compounds of the elements of groups V, VI, and VII, preceding the inert gases in the periodic classification. It may be stated that the postulate of covalency is inapplicable to the majority of the compounds dealt with in inorganic chemistry, with the outstanding exceptions of some compounds of carbon, nitrogen, and oxygen, and that many of the compounds even of these elements possess in all probability not more than one

electron per chemical bond. It cannot even be stated unequivocally that the compounds of organic chemistry usually contain covalency bonds, and much more information must be accumulated before methods can be devised for determining with certainty the number of electrons in the bonds in organic compounds.

The numerous conflicting theories of electron chemical combination to-day alone indicate that the bases of all these theories is insecure. There is Dr. Flūsheim's theory postulating the transmission of affinity or electron demand over a chain of atoms, and denying the existence of alternate polarity and the directing effect of polarity of atoms in substitution processes. There are Professor Fiy's and Vorländer's theories of alternating polarity. There are Professor Lapworth's and Professor Robinson's theories of induced alternate polarities and key-atoms in conjugated systems of double bonds, based also on the covalency and octet theories or modifications of them. There is Professor Lewis's new theory of valency and covalency based on Bohr's dynamic atom. There is Professor Lowry's theory of alternate polarity, crossed polarity, and intramolecular ionisation or half-polarised double bonds, founded on covalency, a modified octet theory, and partly on Bohr's dynamic atom. There is Dr. Sidgwick's non-polar link theory based on covalency and an extension of Bohr's dynamic theory to the combination of atoms. There is Sir J. J. Thomson's theory that a chemical bond may consist of one, two, or three shared electrons, and a host of minor theories based on covalency, the octet theory, and static or dynamic atoms. Professors Thorpe and Morgan both agree that the time is not yet ripe for the application of general electronic theories to organic chemistry.

The failure among chemical theorists to come to agreement about electron combination is to be attributed to a wide variety of causes, e.g., the incorrect assumption in Lewis's theory of invariable covalency combination, the inadequacy of Langmuir's octet theory, and the incorrect-

ness of Bohr's theory of the detailed structures of electron subgroups. Before any generalised theory of chemical combination by electrons becomes possible, some general agreement must be arrived at among chemists as to the type of atom, dynamic or static, to be utilised in chemistry, as to the precise structure of the electron subgroups of this atom, and as to the precise meaning to be attached to the terms polarity, bond, and valence, each of which is used with completely different meanings by different theorists.

In 1921, an amendment of Langmuir's theory of atomic structure was proposed by Bury,<sup>1</sup> who suggested that some of the difficulties in the theory were due to too complete acceptance of Rydberg's series and could be removed by the further postulates that the maximum number of electrons that the outermost shell of an atom can accommodate is eight, that more than eight electrons can be present in an inner shell only when there is an accumulation of electrons in the outermost shell, that groups of eight or eighteen can exist stably in a shell even when the shell can accommodate more than eight or eighteen, and that, where the number of electrons in a shell is increasing from eight to eighteen or from eighteen to thirty-two, the elements concerned can have variable structure and valency, i.e. are the transition elements of the periodic classification. By these postulates Bury was enabled to assign electronic structures to the heavier atoms in closer accordance with their chemical behaviour, particularly as regarded fixed and variable valency. He assumed that the first transition series began with titanium and ended with copper, the second at ruthenium ending with palladium, that the rare earth series of elements began with cerium and ended with lutecium (the then-unknown element actinium or hafnium of atomic number 72 being thus quadrivalent unlike the rare earth elements), and that the third transition series began with osmium and ended with platinum.

The evidence on which Bury based his transition series

<sup>1</sup> *J Amer Chem Soc*, 1921, 43, 1602

was however very incomplete ; he assumed that zirconium, columbium, molybdenum, and silver, were excluded from the second transition series, and tantalum, tungsten, and gold excluded from the third transition series, and thorium and uranium were not placed in a transition series, on the incorrect assumption that all these elements have only one structure and valency. All of these elements, and the fourteen rare earth elements, are properly transition series elements, and, excluding some of the rare earth elements, all of them have variable valency and therefore variable structure.

In 1921, Sir J. J. Thomson<sup>1</sup> put forward a new theory of atomic structure and chemical combination, largely based on his earlier theory of 1914.<sup>2</sup> He endowed the electron groups with stability, impossible in the ordinary classical theory, by postulating a law of force in atoms which changed from attraction to repulsion with approach to the nucleus. By a method of trial and error, he obtained the formula

$$F = \frac{Ne^2}{r^2} \left( 1 - \frac{C}{r} \right)$$

in which  $F$  is the force in the atom between an electron charge  $e$  and a nucleus charge  $Ne$  at a distance  $r$ , and  $C$  is a constant being the distance at which the force changes from attraction to repulsion, and is of the order  $10^{-8}$  cm. (a hundred millionth of a centimetre). This law of force allows eight electrons at the corners of a hypothetical cube to be stably arranged round a nucleus of equal charge. It further allows of the addition of successive shells of eight electrons as the nuclear force increases, thus obtaining structures in which the outside shell never contains more than eight electrons, in conformity with the chemical limitation of valency to eight. In atoms of many shells it was assumed that inner shells could hold more than eight

<sup>1</sup> *Phil Mag*, 1921, [6], 41, 510, *The Electron in Chemistry*, Philadelphia, 1923

<sup>2</sup> *Phil Mag*, 1914, [6], 27, 757

electrons, so that different atoms of high atomic number might have the same valency but a different number of electrons in inner shells, thus accounting for transition series of elements with variable valency.

The theory was applied also to chemical combination by loss or gain of electrons or by sharing of electrons so that the external shells of the reacting atoms all became groups of eight electrons. The evidence of positive ray analysis having proved that a bond of one electron was possible, Sir J. J. Thomson did not feel compelled to adopt the covalency postulate, and in his theory chemical bonds contain numbers of electrons varying from one to four electrons.

Sir J. J. Thomson's theory is an admirable attempt to find a solution for the problem of atomic structure without having to surrender the classical theory of electricity and energy, but it fails to account in any detail for the varying lengths of the periodic groups without special assumptions at each stage, and, being a theory of static electrons, like Langmuir's, it fails to account adequately for the facts of optical and X-ray spectroscopy, for a multitude of general and particular facts in chemistry, and even for some of the facts elucidated by his own positive ray analysis; he quotes the fact that the maximum charge found is eight as confirming his octet structures and the known fact of maximum chemical octavalency, but it is not shown why this maximum charge should occur on the positive particle of mercury, known to have a maximum valency of two, whereas octavalent osmium is the element that ought to have given this charged particle.

In the same year, 1921, Bohr<sup>1</sup> extended his theory of the dynamic atom from the atoms of hydrogen and ionised helium to the elements generally, by allocating to his orbits of total quantum number the numbers of electrons discernible in the various groups of the periodic system. The allocation closely follows the numbers in the shells of

<sup>1</sup> *Fysisk Tidskrift*, 1921, **19**, 153, *The Theory of Spectra and Atomic Constitution*, Cambridge, 1922, *Nature*, 1923, **112**, 29

Langmuir's atoms as amended by Bury. In this scheme the elementary atoms have orbits of quantum numbers 1, 2, 3, 4, 5, 6, and 7, as in the simple hydrogen atom, the maximum numbers in the successive orbits being 2, 8, 18, 32, 18, and 8, up to the orbits of quantum number 6. To account for the inert gases argon, krypton, xenon, and niton, Bohr assumed that an outer group of eight electrons was a stable structure as in Bury's modification of the Langmuir theory. The following are the structures assigned to the inert gases:

TABLE II

Quantum number	-	1	2	3	4	5	6
Helium (2)	-	-	2				
Neon (10)	-	-	2	8			
Argon (18)	-	-	2	8	8		
Krypton (36)	-	-	2	8	18	8	
Xenon (54)	-	-	2	8	18	18	8
Niton (86)	-	-	2	8	18	32	18

From the foregoing it is seen that the 3 quanta group, absent in neon, increases to 8 electrons in passing to argon and then changes to 18 electrons, while the 4 quanta group, absent in argon, increases to 8 electrons in krypton, and that a similar change in the 4 and 5 quanta groups occurs in passing from argon through krypton to xenon, whereas the 4 quanta group further increases from 18 to 32 electrons followed by increase in the 5 quanta group to 18 electrons and the creation of the 6 quanta group with 8 electrons. These changes have been precisely confirmed by the interpretation of the optical and X-ray spectra of the elements immediately following each inert gas, and the reality of these groups and the approximate positions at which change occurs cannot be held to be in doubt. According to Bohr the change of the 3 quanta group commences immediately after calcium (20), in which the energy of the 4 quanta valency electrons is only very slightly greater than that of the inner 3 quanta electrons, and that scandium (21) has the same valency, the additional electron going to

increase the 3 quanta group from 8 to 9 electrons, and that successive elements continue to add electrons to the inner group till it has the full quota of 18 electrons as in the cuprous ion, the transition series thus consisting of 9 elements from scandium to copper.

Similarly the second transition series extends from yttrium (39) to silver (47).

After barium (56) Bohr assumes that the next electron goes to the 5 instead of the 6 quanta orbits, as in lanthanum (57), but that the next electron goes to the 4 quanta orbits in cerium (58), and that the next 13 electrons also go to the 4 quanta orbits, thus forming the rare earth group of 14 elements from cerium to lutecium (71), in which the 4 quanta group of 32 electrons is complete. Further addition of electrons then occurs in the 5 quanta orbits, from cerium (72) to gold (79), in which the 5 quanta orbit is complete with 18 electrons. Further addition of electrons then occurs in the 6 quanta group till 8 electrons are added as in radon (86). Only three more chemical elements are known, radium (88), thorium (90), and uranium (92), and Bohr assumes that these elements are in a periodic group of 32, which, like the previous group of 32, includes a long transition series commencing with the trivalent element of atomic number 89 (actinium if admitted as a chemical element).

The foregoing scheme gives a very complete explanation of the form of the periodic classification, and is supported at the critical points by very strong spectroscopic evidence, and in outline this scheme of atomic structure must be accepted as a reality.

In order to account for the fact that the X-ray emission spectra provide for two orbits of quantum number 2, three of quantum number 3, four of quantum number 4, three of quantum number 5, and two of quantum number 6, Bohr divided the various quantum group electrons into sub-groups characterised by the azimuthal quantum numbers proposed by Sommerfeld. The question then arose as to

how many of the group electrons should be placed in each subgroup. Obviously the first quantum group from hydrogen (1) to helium (2), which consists of only one group of 2 electrons in helium, must supply the answer if any general law underlies the formation of subgroups. Bohr noticed that this group, with quantum number 1, has only 1 group of 2 electrons or double the total quantum number. Bohr's guess consisted in the assumption that this constituted the subgroup law, particularly as it gave symmetrical arrangements to all the quantum groups, the 1 quantum group having 1 group of  $2 \times 1 = 2$  electrons, the 2 quanta group 2 subgroups each of  $2 \times 2 = 4$  electrons, the 3 quanta group 3 subgroups each of  $2 \times 3 = 6$  electrons, and the 4 quanta group 4 subgroups each of  $2 \times 4 = 8$  electrons. This law is that the maximum number of subgroups is equal to the total quantum number, and the maximum number of electrons in a subgroup is equal to twice the total quantum number.

It will be shown in the next chapter that Bohr's subgroups do not fit chemical facts. It inevitably gives symmetrical arrangements because the total number of electrons in a group is twice the square of the total quantum number, i.e. Rydberg's series, the unsquared numbers of which are accidentally the same as Bohr's total quantum numbers. It is obvious that the square of a number is symmetrically divisible by the number. It is unfortunate that Bohr was misled by a numerical coincidence and the properties of numbers, because his subgroup scheme has been made the basis of theories of chemical combination which come near enough to agreeing with chemical facts to make them a valid expedient in chemistry, and have led only to a non-concordant interpretation of chemical problems of atomic and molecular structure and the mechanism of electronic combination.

In 1923, Sidgwick<sup>1</sup> put forward a theory of chemical

<sup>1</sup> *J. Chem. Soc.*, 1923, 123, 725, *Brit Assoc' Rep.*, 1923, *Chem Ind.*, 1923, 42, 901

combination based on Bohr's subgroup scheme and the covalency theory of chemical bonds in non-ionising compounds. He assumed that every chemical bond in every type of compound consists of two shared electrons, which go to complete in each atom two of the subgroups of Bohr's scheme, though no reason is advanced as to why only two completed subgroups confer stability on atomic structures, when there are three possible subgroups for 3 quanta orbits, four subgroups for 4 quanta orbits, and only one subgroup for 1 quantum orbits. The criticism already advanced in earlier chapters, as to the general inapplicability of the covalency of two electrons per chemical bond applies with even greater force to theories based on Bohr's subgroup scheme than to those based on an octet scheme, for the outermost subgroups throughout the scheme never contain more than six electrons. Sidgwick's theory is consequently frequently inapplicable to the whole of the elements preceding the inert gases in which the non-ionising valency or the co-ordination number is greater than three. This includes almost the whole of the known elements. The aluminium atom in cryolite,  $\text{AlF}_6\text{Na}_3$ , for example, must have four more electrons than the next higher inert gas. The covalency postulate, in fact, can be maintained only by excluding the inert gases from the atomic structures of maximum inertness and stability. A similar argument applies to all hydrogen compounds assigned a covalency of two, such compounds having in consequence two more electrons than the nearest inert gas helium, which, in common with the other inert gases, Sir J. J. Thomson's positive ray analysis has proved, is incapable of acquiring any additional electrons whatever.

Though Sidgwick's theory is based on the incorrect subgroups of Bohr's scheme, and on the incorrect assumption of invariable covalency bonds, he has supplied the elucidating key of a simple rule for determining the probable outer structures of the majority of complex and co-ordinated compounds. This rule states that the maximum

covalency or co-ordination number is equal to the maximum possible number of electrons in a valency subgroup, next to the largest completed group in the atom. This rule, divorced from covalency, is a particular case of the general law of uniform atomic plan, which was deduced in Chapter X from the phenomena of radioactivity and the relations between the periodic groups. This law may be stated in more precise terms, including the atomic phenomena summarised in the Bohr-Sommerfeld dynamic atom, that all atoms are constructed on the same uniform atomic plan, and that for every total quantum number in an atom, there is the same maximum number of electronic orbits of the same shape and distribution in space, each containing the same maximum number of electrons, shared or unshared with other atoms. This law has been the basis, in one or more of its particular applications, of the whole of the theories of atomic structure, and was dimly apprehended by Mendeléeff, more clearly apprehended by Rydberg, still more clearly by Rutherford, Sir J. J. Thomson and Langmuir, almost grasped by Bohr, and is the key to Sidgwick's rule of electronic chemical combination.

## ATOMIC STRUCTURE AND THE CHEMICAL PROPERTIES OF ELEMENTS

BOHR's theory of atomic structure is strictly a theory relating to single atoms, neutral or ionised, far removed from the influence of other atoms. The fact that it is an interpretation of the periodic classification of the elements, largely based on the properties of atoms in combination, indicates that it must be valid for atoms in combination, at least so far as the broad outlines of the theory are concerned. The theory certainly necessitates that the general type of the structure of an atom is preserved even when the atom loses some of its electrons, and thus acquires positive charges. This is confirmed by the spectroscopic law of periodic group displacement, that the optical spectrum of an element that has lost one electron resembles closely the spectrum of the element one less in atomic number, and that the spectrum of an element that has lost two electrons resembles closely the spectrum of the element two less in atomic number. This is further confirmed by Moseley's spectroscopic law connecting the wave-length of X-radiation with atomic number and with quantum conditions of atoms, the various quantum conditions being unchanged in atoms in combination. It may therefore be accepted that the structure of an atom is not influenced in qualitative aspects and only slightly in quantitative aspects by chemical combination. In general it may be assumed that chemical combination between atoms is powerless to alter more than the external portions of the structure of atoms, and that this alteration occurs in or near the electrons of the structure which are known as valency electrons.

One of the outstanding periodic properties of atoms in general is their tendency to yield compounds which are alkaline, acid, or amphotERICALLY neutral. An examination of the periodic system indicates that the property of alkalinity is intense for the univalent alkali metals and is less intense for the bivalent alkaline earth metals, and

suddenly disappears in the trivalent elements boron, aluminium, gallium, etc., and does not appear elsewhere in the periodic classification, increasing acidity being observed as the periods are traversed.

It is further a noticeable property of the tivalent elements of group III to yield compounds containing two valences, co-ordinated or non-ionising, and one unco-ordinated or ionising valence, and that the property of two co-ordinated valences is common to the whole of the quadrivalent elements of group IV, and persists to a considerable extent in the elements of groups V, VI, and VII, and that this property is only observable when the elements are acting electropositively, i.e. when oxidised or partly deprived of electrons. This may be interpreted as evidence that all elements containing more than two valency electrons have two electrons more firmly attached than other valency electrons, which, further interpreted in terms of orbits, indicates that two electrons in the outer structure of atoms are in quantum orbits the energies of which are different from that of other outer electrons. This is directly confirmed by the well-known spectroscopic fact that the outer orbits of the aluminium atom with three valency electrons are of two different energy types, and that the spectra of tivalent elements generally bear considerable resemblance to the spectra of univalent elements.

Corresponding observations on the property of acidity of elements indicate that it is a maximum in group VII and diminishes only gradually in groups VI and V, and suddenly changes to perceptible basicity or at least amphotericity in group IV. It is further notable that nearly all of the elements of these groups have a marked tendency to yield compounds having the co-ordination number 4, independently of the number of ions with which the co-ordination complex may be associated. This may be interpreted as evidence that the valency electrons in excess of four are all equally feebly attached to the atoms, which, further interpreted in terms of orbits, indicates

that the valency electrons in excess of four are all in similar quantum orbits the energy of which is less than that of the first four electrons.

The detailed chemical evidence, by which it can be shown that the first two valency electrons are differentiated in energy or firmness of binding from the third and fourth electrons, and that both of these pairs are differentiated from the remaining valency electrons, is so vast that no more than a tithe of this evidence need be cited to prove the point.

Cupric salts yield characteristically insoluble and stable di-pyridino-compounds, gold the dyad symmetrical di-alkyl auric salts and thallium the similar di-alkyl thallic salts. The reactivity of the magnesium Grignard reagents is attributable to the unsymmetrical valencies.

Dyad symmetry is also evident in the chain structure of the valencies of such atoms as boron in the hydrides, carbon in organic compounds, nitrogen in polyazo-compounds, silicon in the silico-hydrocarbons, sulphur in polythionates and polysulphides, selenium in the seleno-dithionates<sup>1</sup> and, further, in such compounds as carbon monoxide, ketones, aldehydes, and other carbonyl derivatives, also in *gem*-dialkyl groups attached to carbon, nitrogen, phosphorus, arsenic, antimony, tin, and tellurium atoms. Boron acetylacetone fluoride has the simple formula,  $\text{BF}_2\text{Ac}$ , not the complex formula  $[\text{BF}_4][\text{BAc}_2]$ ,<sup>2</sup> and only one of the three chlorine atoms in aluminium chloride is displaced in the Friedel-Craft's reactions.

Chlorates, bromates, and iodates, are readily formed and furnish perchlorates, perbromates, and periodates only with difficulty. Nitrogen and arsenic yield no pentachlorides, and phosphorus and arsenic pentafluorides readily yield free fluorine on heating. Selenic, arsenic, perbromic, and bismuthic compounds are not readily formed by ordinary oxidations.

The foregoing relate entirely to the "odd" periodic series. The trivalent elements of the "even" series,

<sup>1</sup> Morgan and Drew, *J Chem Soc.*, 1921, 117, 1456, Morgan and Main Smith, *J Chem Soc*, 1921, 119, 1066,

Morgan and Tunstall, *J Chem Soc*, 1924, 125, 1963

scandium, yttrium, lanthanum, and the "rare earths" have all three valency electrons equivalent, due to the fact that the third electron is in a group of lower quantum number and possesses the same energy. This equal firmness of binding for different quantum orbits has been directly deduced from X-ray spectra.

It may therefore be regarded as certain that the first three subgroups of any total quantum number consist of 2, 2, and 4 electrons.

If the types of quantum orbits persist in atoms with increase in atomic number, it must be concluded that the valency subgroups discernible in the atoms from lithium to neon, persist in the succeeding 3 quantum group also of 8 electrons, and that this grouping of 2, 2, 4 electrons is preserved in the inner groups of the atoms from sodium to argon, which certainly possess this grouping in their outer valency electrons.

By similar arguments the succeeding elements also possess these groups of 2, 2, 4 electrons, and it is known from Millikan's<sup>1</sup> work on the spectra of multiply-ionised atoms that the helium structure of 2 electrons is preserved in the elements from lithium to sodium, and that the neon structure is preserved in the elements from sodium to argon. This has recently been fully confirmed by Dauvillier's<sup>2</sup> work on the widths of the X-ray spectral absorption bands of heavy metals for the L or 2 quanta spectral series. Dauvillier found that the relative widths of the bands, which are accepted to be due to the number of energy-absorbing electrons in the atom, are in the ratio of 1 : 1 : 2, and as there are 8 L electrons, the numbers in each subgroup must be 2 : 2 : 4, as indicated by the foregoing chemical evidence.

This evidence shows conclusively that Bohr's subgroup scheme, of two subgroups of 4 electrons for the 2 quanta group, cannot be maintained. His postulate of three sub-

<sup>1</sup> Faraday Lecture, *J. Chem. Soc.*, 1924, 125, 1405

<sup>2</sup> *Compt. rend.*, 1924, 178, 476

groups for the 3 quanta electrons also cannot be maintained for the absorption spectral evidence indicates that there are five subgroups in the quantum group. The same evidence also indicates that the postulate of four subgroups for the 4 quanta electrons can not be maintained, for seven subgroups are discernible in the spectra. Bohr's rules that the number of subgroups is equal to the quantum number and that the number of electrons in a subgroup is equal to twice the quantum number are therefore both incorrect. It is remarkable, when Bohr devised his subgroup scheme and characterised the subgroups by total and azimuthal quantum numbers, that he did not discern something of the meaning of the variable factor in the quantum scheme, i.e. the increase in the azimuthal quantum number in the subgroups, and that he failed to realise the importance of the evidence of absorption spectra in his scheme of atomic structure.

The complete scheme of notation for the X-ray spectra is  $1_1a, 2_1b, 2_1a, 2_2a; 3_1b, 3_1a, 3_2a, 3_2b, 3_3b, 4_1b, 4_1a, 4_2a, 4_2b, 4_3b, 4_3a, \text{ and } 4_4a$ . The notation used in Bohr's atomic structures is  $1_1; 2_1, 2_2; 3_1, 3_2, 3_3; 4_1, 4_2, 4_3, \text{ and } 4_4$ . It will be observed that the former scheme is derived from the latter by dividing all the orbits corresponding to ellipses into two types a and b, or, in other words, in subdividing into two all orbits having radial quantum number, the circular orbits, in which the total and azimuthal quantum numbers are equal, not being affected. It will also be observed that the resulting number of orbital types or subgroups, for the quantum numbers 1, 2, 3, and 4, is 1, 3, 5, and 7, or one less than twice the total quantum number, i.e. the number of subgroups =  $2n - 1$ .

The foregoing chemical evidence indicates that the first quantum group is a single subgroup of 2 electrons, and that the second quantum group consists of 3 subgroups containing 2, 2, and 4 electrons. It may now be observed that the number of subgroups is in fact equal to one less than twice the group number, in conformity with the

spectral evidence. The numbers 2, 2, 4 are further identifiable as twice the azimuthal quantum number, so that the rule for the number of electrons in a subgroup is  $2k$ , where  $k$  is the azimuthal quantum number. This indicates that the electrons in the 3 quanta subgroups are, in order, 2, 2, 4, 4, and 6, being five subgroups, and that the numbers in the 4 quanta orbits are 2, 2, 4, 4, 6, 6, and 8, or seven subgroups. The law of uniform atomic plan may therefore be regarded as established, and has thus been deduced from the evidence of radioactivity, the evidence of the periodic classification, the evidence of general and specific chemical properties including valency and co-ordination, the evidence of the widths of X-ray absorption bands, the evidence of the wave-lengths of optical spectra, the evidence of the wave-lengths of X-ray emission spectra, and the evidence of the wave-lengths corresponding to the heads of the bands of X-ray absorption spectra. It may further be remarked that the evidence of the total intensity of the lines of X-ray emission spectra is to the same effect; in the L series the total intensity of the lines due to circular orbits is 24, and the average intensity of the two series of lines due to elliptic orbits is about 11, a ratio of approximately 4 to 2; the total intensity of the lines due to circular orbits in the M series is 10, and the average intensity of the lines due to elliptic orbits is 4, a ratio of  $2\frac{1}{2}$  to 1, whereas the ratio of the electrons in circular to elliptic orbits is actually 2 to 1.

The establishment of the law of uniform atomic plan on the foregoing considerations renders it unnecessary to cite the further chemical evidence by which it can be shown that the electrons in the 3 quanta group actually are disposed in subgroups of 2, 2, 4, 4, and 6, but it may be remarked that the law was deduced from this evidence before the rule of doubling Sommerfeld's azimuthal quantum number had been appreciated, and indicates how complete is the chemical evidence as to atomic structure, despite the usual dictum that chemistry has concern only with

the peripheral properties of atoms, i.e. with their valency electrons.

The chemical evidence, as to the precise points in the periodic classification at which added electrons go into interior groups and into what subgroups, and as to the numbers of electrons entering the various subgroups, is not quite so precise, but it indicates that the first transition series commences with scandium as in Bohr's scheme; that the second transition group commences at yttrium; and the third at lanthanum. It further indicates that the fourth 3 quanta subgroup commences to be filled at manganese; that the fourth 4 quanta group commences to be filled at ruthenium, and the sixth at europium; that the fifth and fourth 5 quanta groups commence to be filled at cerium and osmium respectively, and that the fourth 6 quanta group commences to be filled at actinium.

The structures of the various atoms at the several critical points in the periodic and quantic classifications are given in the subjoined tables, and these may be regarded as expressing with considerable accuracy the atomic structures of the whole of the known elements as deduced largely from the idiosyncratic properties of atoms ascertained in chemistry.

TABLE 12  
GENERAL SCHEME OF ATOMIC STRUCTURE

Total quantum number			1		2	3	4	5	6
Azimuthal quantum number			1		112	11223	1122334	11223	1122
He (2)	-	-	-	2					
Gl (4)	-	-	-	2	2				
C (6)	-	-	-	2	22				
Ne (10)	-	-	-	2	224				
Ar (18) and Sc <sup>3</sup> (21)	-	2	224	224					
Cu <sup>1</sup> (29)	-	-	-	2	224	22446			
Kr (36) and Y <sup>3</sup> (39)	-	2	224	22446	224				
Ag <sup>1</sup> (47)	-	-	-	2	224	22446	22446		
Xe (54) and La <sup>3</sup> (57)	-	2	224	22446	22446	22446		224	
Lu <sup>3</sup> (71)	-	-	-	2	224	22446	2244668	224	
Au <sup>1</sup> (79)	-	-	-	2	224	22446	2244668	22446	
Nt (86)	-	-	-	2	224	22446	2244668	22446	224
U <sup>2</sup> (92)	-	-	-	2	224	22446	2244668	22446	2244

TABLE 13  
TRANSITION SERIES I

Total quantum number			n= 1		2	3							
Azimuthal quantum number			l= 1		112	112	23	23	23	23	23	23	23
Valency of ion			—	—	—	1	2	3	4	5	6	7	
Sc (21)	-	-	2	224	224	—	—	00					
Ti (22)	-	-	2	224	224	—	02	01	00				
V (23)	-	-	2	224	224	—	03	02	01	00			
Cr (24)	-	-	2	224	224	—	04	03	—	01	00		
Mn (25)	-	-	2	224	224	—	14	13	12	—	10	00	
Fe (26)	-	-	2	224	224	—	24	23	—	—	20		
Co (27)	-	-	2	224	224	—	25	24	23				
Ni (28)	-	-	2	224	224	—	26	—	24				
Cu (29)	-	-	2	224	224	46	45	44					

TABLE I4  
TRANSITION SERIES 2

Total quantum number $n=$		1	2	3	4							
Azimuthal quantum number $k=$		1	112	11223	112	23	23	23	23	23	23	23
Valency of ion		—	—	—	—	1	2	3	4	5	6	7 8
Y (39) -	-	2	224	22446	224	—	—	00				
Zr (40) -	-	2	224	22446	224	—	02	01	00			
Cb (41) -	-	2	224	22446	224	—	03	02	01	00		
Mo (42) -	-	2	224	22446	224	—	04	03	02	01	00	
— (43) -	—	—	—	—	—	—	—	—	—	—	—	—
Ru (44) -	-	2	224	22446	224	—	24	23	22	—	20	10 00
Rh (45) -	-	2	224	22446	224	—	25	24	23	—	21	
Pd (46) -	-	2	224	22446	224	—	26	—	24			
Ag (47) -	-	2	224	22446	224	46	45					

TABLE I5  
TRANSITION SERIES 3A

Total quantum number $n=$		1	2	3	4				5
Azimuthal quantum number $k=$		1	112	11223	11223	34	34	34	112
Valency of ion		—	—	—	—	2	3	4	—
La (57) -	-	2	224	22446	22446	—	00	—	224
Ce (58) -	-	2	224	22446	22446	—	01	00	224
Pr (59) -	-	2	224	22446	22446	—	02	01	224
Nd (60) -	-	2	224	22446	22446	—	03	—	224
— (61) -	—	—	—	—	—	—	—	—	—
Sa (62) -	-	2	224	22446	22446	06	05	—	224
Eu (63) -	-	2	224	22446	22446	16	15	—	224
Gd (64) -	-	2	224	22446	22446	—	16	—	224
Tb (65) -	-	2	224	22446	22446	—	17	16	224
Dy (66) -	-	2	224	22446	22446	—	18	—	224
Ho (67) -	-	2	224	22446	22446	—	28	—	224
Er (68) -	-	2	224	22446	22446	—	38	—	224
Tm (69) -	-	2	224	22446	22446	—	48	—	224
Yb (70) -	-	2	224	22446	22446	—	58	—	224
Lu (71) -	-	2	224	22446	22446	—	68	—	224

TABLE 16  
TRANSITION SERIES 3B

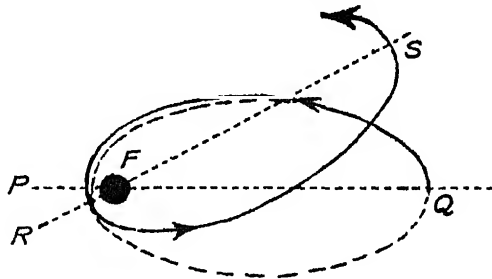
Total quantum number $n =$	1	2	3	4	5								
Azimuthal quantum number $k =$	1	112	11223	1122334	112	23	23	23	23	23	23	23	23
Valency of ion	—	—	—	—	—	1	2	3	4	5	6	7	8
Ct (72)	-	2	224	22446	2244668	224	—	—	—	00			
Ta (73)	-	2	224	22446	2244668	224	—	03	02	01	00		
W (74)	-	2	224	22446	2244668	224	—	04	03	02	01	00	
— (75)	-	—	—	—	—	—	—	—	—	—	—	—	—
Os (76)	-	2	224	22446	2244668	224	—	24	23	22	—	20	— 00
Ir (77)	-	2	224	22446	2244668	224	—	25	24	23	—	21	
Pt (78)	-	2	224	22446	2244668	224	—	26	—	24	—	22	
Au (79)	-	2	224	22446	2244668	224	46	—	44				

## APPENDIX

### THE "RELATIVITY EFFECT" ON MASS

BOTH the classical theory and the theory of relativity postulate that continuous increase in mass accompanies continuous increase in the velocity with which the mass moves. Any portion of matter, therefore, decreasing its distance from an attracting force and consequently increasing its velocity, must undergo increase of mass. If the attracting force is due to electric charges of fixed quantity, the force causing motion will not depend upon the mass to be moved. If this mass has increased the unchanging charges cannot move the larger mass with the same velocity, the velocity of the new mass consequently falls off, and the movement of the mass is retarded. If the mass were originally travelling in an orbit subject to a constant central force, increase of mass must be accompanied by increase in the radius of the orbit. Conversely, decrease in mass must be accompanied by decrease in the radius of the orbit. The velocity of a body in an elliptic orbit, with the centre of attraction at one focus, must increase as the body moves from aphelion further away to perihelion nearer the nucleus, and in consequence the mass of the body must increase with approach to perihelion and decrease with approach to aphelion. The increase of mass must involve increase of orbital radius and the decrease of mass involve decrease of orbital radius. The real path of a massive body in an initially elliptic orbit thus lies further away than a true ellipse in approaching, and nearer in receding from the focus. In Diagram XVII, the

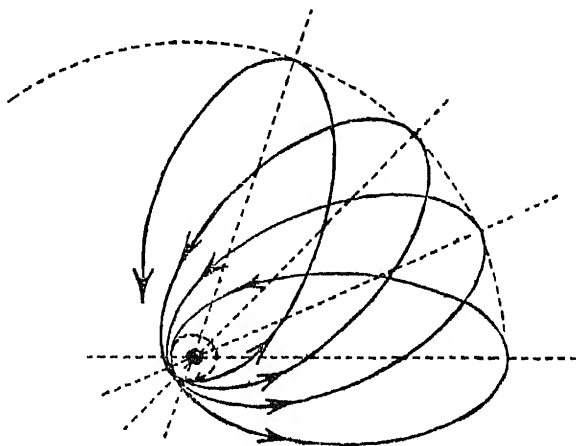
DIAGRAM XVII



elliptic orbit of a massless particle is shown dotted, the full line representing the actual path of a massive particle. It will be seen that the original major axis, PQ, of the orbit is turned through the angle, SFQ, in one revolution, and that the rotation of the axis is

in the same clock-wise direction as the circulation in the orbit. Diagram XVIII shows successive positions of the axis with successive revolutions in the orbit, the aphelion describing a circle of radius equal to the aphelion distance from the focus, and the perihelion a

DIAGRAM XVIII



smaller circle of radius equal to the perihelion distance from the focus. The actual orbit described by the particle is that due to the confocal superposition of a circular motion on an elliptic motion in the same plane.

Sommerfeld's postulate that an electron circulating about a nucleus can describe elliptic as well as circular orbits, involved the extension of velocity-mass-effects to electrons in atoms, and the foregoing diagrams may be regarded as expressing, on an exaggerated scale, the effect in elliptic orbits, i.e. orbits having both radial and azimuthal quantum numbers. He predicted that the more eccentric orbits (having smallest azimuthal quantum numbers) would exhibit the greatest mass increase, and thus possess greatest energy, and that, consequently, every possible elliptic orbit would give rise to a separate line in spectra, both optical and X-ray. This prediction has been abundantly confirmed in the "fine-structure" of spectral lines, and electrons with mass varying with velocity must therefore be accepted as realities in atomic structure.

The circular motion of the whole elliptic orbit about the focus is described as a precession motion in the plane of the orbit, and is

Sommerfeld's "relativity effect." It is obvious that the foregoing considerations as to planar precession can apply only to an electron completely unperturbed in its motion by other forces. The introduction of another electron into the system must perturb the precession motion profoundly. Several electrons about the focus must still further perturb the precession, and if all the electrons are similar in type and undergo similar precession, the mutual interpenetration will render normal plane precession impossible; yet precession must occur, must occur symmetrically and to the same extent for all similar electron orbits, and must not be materially altered by the addition of further electrons in other precessing orbits of different type. This can be achieved, as indicated on p. 174, Chap. XII, if the plane, in which precession occurs, rotates about the fixed major axis of the elliptic orbit, the electron thus describing spiral paths between a fixed perihelion and aphelion on the surface of an ellipsoid of revolution, each electron in an atom of whatever total or radial quantum number thus appropriating a small ellipsoidal domain around a radius of a sphere with the nucleus as centre.

The spatial "relativity effect" above described consists of the superposition of a circular motion on an elliptic motion not in the same plane. It differs from Sommerfeld's relativity effect only in the plane of superposition. It extends the plane conception of simple atoms to the spatial conception of complex atoms, just as modern chemistry is a spatial interpretation of the old chemistry in a plane.

Electron orbits in free atoms are "borgne," "one-eyed," have a nucleus only at one focus of the orbit. Atoms, however, which enter into chemical combination and remain indissolubly attached to one another, as in non-ionisable compounds and co-ordination compounds generally, are in another category—their electron orbits are "two-eyed," and, according to the most recent views, some of the electrons, valency electrons, circulate round both atomic nuclei in orbits common to both atoms. Obviously as such orbits have two foci of attracting nuclear charges, electrons cannot describe elliptic orbits nor yet circular orbits, both of which are characteristic of orbits with a single central force. Professor G. T. Morgan came to the conclusion some years ago that the closed curves, known to mathematicians as "ovals of Cassini," which are "two-eyed," might suffice to represent the orbits of shared electrons. The Cassinian system of curves is such that the product of the distances from the

foci of a point on a curve is constant. Clerk Maxwell, in his *Electricity and Magnetism*, 1873, showed that the sections of equipotential surfaces about two equal similar charges were Cassinian ovals. It follows, therefore, that a Cassinian oval is an orbit of constant potential, and, consequently, a possible Bohr orbit for an electron. Some of the Cassinian ovals are shown in Diagram XX, page 204, which represents a series of Bohr orbits of shared electrons. The outer ovals are nearly elliptic, the median curve, figure-of-eight, is known as the lemniscate of Bernoulli, and the inner separated curves approach circles as the foci are approached.

The figure-of-eight curve has been independently suggested by Professor Lowry, as representing cases of shared-electron orbits. In Professor Morgan's view the figure-of-eight or lemniscate curve is the limiting case of such electron-sharing, and represents an atom on the verge of becoming a free ion by loss or gain of the shared electron, the smallest alteration in force sufficing to send the electron into one or other of the "inner ovals." This view has been one of the mainsprings and guiding principles of his direction of the Birmingham research school in the last three or four years, and has been applied with success to the explanation of all easily-hydrolysable organic and inorganic compounds. The chief objection to the Cassinian system of orbits is that they are incompatible with relativistic change of mass with velocity.

It was suggested in the Faraday Society's general discussion on the electronic theory of valency (1923), that the figure-of-eight curve allows for the "relativity effect," on the ground that "*the outward loop cuts the preceding inward loop instead of being superposed upon it. This is precisely what happens in the figure-of-eight.*" This statement is correct but misleading. Many orbits have similar loop-cutting properties, but they are not in consequence able to accommodate a relativistic change of mass with change in velocity.

The figure-of-eight curve is merely the lemniscate and a special case of Cassinian oval. The Cassinian system is derived from the superposition of two co-planar non-concentric circular motions, and thus is fundamentally different from Sommerfeld's relativity effect of a superposition of a circular motion on a confocal co-planar elliptic motion. The "relativity effect" necessitates the rotation of the orbital axis in the orbit plane about the focal centre. The Cassinian system cannot be rotated in the orbit plane about the focal centre because there are two foci. Rotation about either

focus must rotate the whole other atom or the Cassinian system will be ruptured. The actual path of an electron exhibiting relativity effect is indicated in Diagram XIX, the orbit being initially the figure-of-eight. After one revolution the electron leaves the

### DIAGRAM XIX

*Electron Precession Orbit changing continuously from Figure-of-Eight to Rectilinear Vibration*

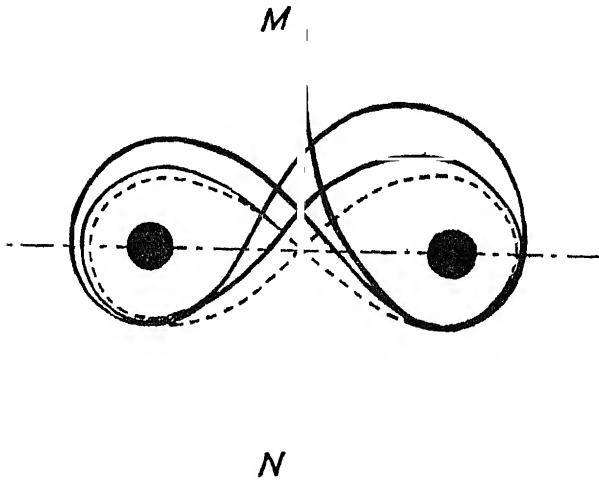


figure-of-eight and enters an outer oval, and after a few revolutions in a deforming and expanding figure-of-eight, finally travels tangentially to the median line MN, and continues to vibrate to and fro on this line indefinitely. In general, it may be stated that an orbit allowing for relativistic change of mass with change of velocity cannot exist in the orbital plane, where the force causing motion is directed from more than one point. This applies to two electrons about one nucleus, equally as to one electron about two nuclei.

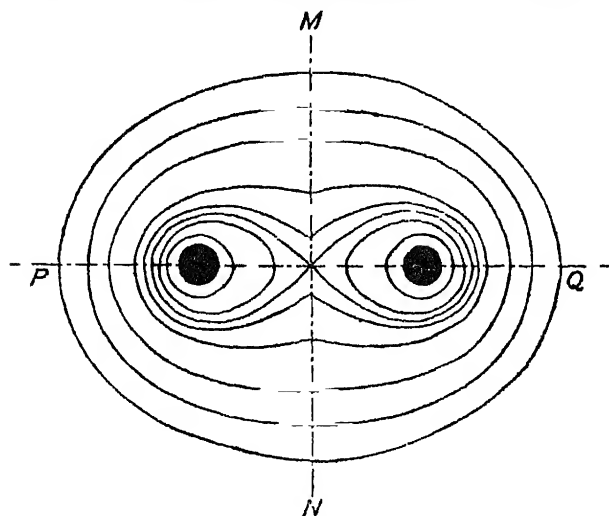
The difficulty is overcome by allowing precession to take place in a plane other than the orbital plane, as with a single atom with several electrons (see p. 174). The whole Cassinian system on revolution about the horizontal axis describes a series of confocal surfaces which are Cassinian ovals of revolution, the surfaces being in fact Clerk Maxwell's equipotential surfaces. Any Cassinian oval of revolution must comprise all possible Bohr orbits, for the potential

is constant at all points. All such orbits, described spirally between the two fixed perihelion points, allow for "relativity effect."

It may be pointed out that, strictly, the question of "relativity effect" is not applicable to Cassinian orbits, for they are derived from the superposition of two circular orbits, i.e. relate to the conjoint orbit of two circular orbits, to neither of which relativistic

### DIAGRAM XX

*Oval Orbit about Two Atomic Nuclei at the Foci of a Cassinian System*



change of mass applies. The system, to which elliptic orbits conform on superposition, is not the true Cassinian system, but the harmonic curves resulting from the superposition of two elliptic orbits. This system, which may be termed the elliptic Cassinian system, does not appear to have been investigated in detail by mathematicians. It is however the system of orbits common to two atoms in which electrons rotate that would have elliptic orbits in either atom separately. Spatial precession may be readily applied to such orbits, the motion of the electron being the superposition of a coaxial circular motion on two superposed non-confocal coplanar coaxial elliptic motions. Obviously a similar spatial circular precession can be applied to a circular orbit superposed on a non-confocal co-planar elliptic orbit, thus representing the orbit of an

electron which in one atom separately would be circular and in the other elliptic.

An electron travelling from an inner to an outer orbit of superposed simple harmonic motions of the foregoing types, will give rise to light radiation in which these superposed motions will be components in the light vibration, and will give rise to spectral lines according to the nature of the composite initial and final types of orbital motion, thus giving a clue to the meaning of Bohr's "correspondence principle," in which the various types of emitted radiation are likened to the overtones and harmonics of the musical scale, the frequency of every spectral line, even those produced by external forces as in the Stark and Zeeman effects, being related to a corresponding vibration frequency in orbital motion of electrons.



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